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PROCESS ENGINEERING DESIGN FOR MANUFACTURE OF  
GUANIDINE NITRATE

HERCULES, INC.

PREPARED FOR  
PICATINNY ARSENAL

AUGUST 1973

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PROCESS ENGINEERING DESIGN FOR MANUFACTURE OF GUANIDINE NITRATE

Final Report

APPENDICES FOR VOLUME I

(Unclassified - Department of the Army)

N. W. Steele  
J. A. Doyle  
M. G. Whippen

August 1973

Prepared for

DEPARTMENT OF THE ARMY  
PICATINNY ARSENAL  
Dover, New Jersey 07901

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The findings in this report are not to be construed  
as an official Department of the Army position.

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## APPENDIX I - PHASE I

### LABORATORY, ENGINEERING, ECONOMIC AND TECHNOLOGY STUDIES

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## APPENDIX I-1

### PACKED BED REACTOR MODEL

In this section, a detailed description of the packed bed reactor model is given. The method of numerical solution of the ordinary and partial differential equations is also treated.

#### Model Development

The model for the packed bed reactor is based upon material and energy balances for the system. By considering an annular ring of differential size, the following ordinary and partial differential equations for the concentrations and temperature at every point in the reactor may be written:

$$(1) \frac{dN_{GN}}{dz} = \frac{1}{L} \left[ R_{GN} \cdot \rho \cdot A - N_{GN} \frac{dL}{dz} \right]$$

$$(2) \frac{dN_{H_2}}{dz} = \frac{1}{L} \left[ R_{H_2} \cdot \rho \cdot A - N_{H_2} \frac{dL}{dz} \right]$$

$$(3) \frac{dN_{H_2O}}{dz} = \frac{1}{L} \left[ R_{H_2O} \cdot \rho \cdot A - N_{H_2O} \frac{dL}{dz} \right]$$

$$(4) \frac{dL}{dz} = R_{H_2} \cdot \rho \cdot A$$

$$(5) \frac{dG}{dz} = 3 \cdot R_{GN} \cdot P_B \cdot A$$

(Gas actually 2 NH<sub>3</sub>  
+ CO<sub>2</sub> & not PC;  
R<sub>G</sub> = 3 R<sub>un</sub>)

$$(6) K_E \left[ \frac{d^2 T}{dz^2} + \frac{1}{r} \frac{dT}{dz} \right] - \phi \frac{dT}{dz} - \psi (T - T_1) \\ = H_R \cdot R_{GN} \cdot P_B$$

where

$$(7) R_{GN} = N_u \cdot N_{AN} \cdot k_{un}^0 e^{-E_{un}/RT_{avg}}$$

$$(8) R_u = -N_u^2 \cdot N_{AN} \cdot k_{u1}^0 e^{-E_{u1}/RT_{avg}}$$

$$(9) R_{AN} = -R_{GN}$$

$$(10) \phi = C_L \cdot L' + C_G \cdot G'$$

$$(11) \psi = C_L \cdot \frac{dL'}{dz} + C_G \cdot \frac{dG'}{dz}$$

$$(12) N_{un} + N_u + N_{AN} = 1$$

$$(13) T_{avg} = \frac{2\pi}{A} \int_0^r T(r) \cdot r \cdot dr$$

The definition of the variables used in these equations can be found in the List of Symbols included at the end of this section.

Equations (1), (2), and (3) are the material balances for guanidine nitrate, urea, and ammonium nitrate and describe the variation in mole fraction for each component in the axial direction. The mole fractions have been assumed uniform in the radial direction. This is a reasonable assumption in packed bed operations since the catalyst particles contribute to a lateral movement of fluid leading to mixing in the radial direction. In addition, the time associated with convective transport of material in the axial direction will far outweigh any contribution due to radial concentration gradients. The first term on the right-hand-side of Equations (1), (2), and (3) accounts for the production or removal of material by chemical reaction. The rate expressions used here and defined by Equations (7), (8), and (9) are those obtained through the analysis of the kinetic experiments of this project as presented in last month's report. The second term in the material balance equations accounts for the effect of the change in melt volume due to chemical reaction on the variation in mole fraction with axial position. Equation (4) is obtained by summing Equations (1), (2), and (3) and recalling that Equation (12) also applies. Equation (5) describes the rate of production of gas as a function of axial position and assumes that the gas is generated only by those reactions that



produce guanidine nitrate, and that an insignificant amount of gas is generated by side reactions. This is in keeping with the experimental results of this project in which no gas other than that going to ammonium carbamate was detected.

Equation (6) is the energy balance for the packed bed reactor and describes both the radial and axial variation in temperature. Axial and radial temperature profiles are important, since the reaction rates are a strong function of temperature. The yields, conversions, and concentration profiles will be directly affected. In addition, the maximum allowable radial temperature difference will determine the maximum diameter of the packed bed reactor.

The first term in Equation (6) accounts for the energy transfer in the radial direction by conduction. All resistances to heat transfer in the radial direction inside the bed are included in the effective thermal conductivity,  $K_E$ . These resistances include thermal resistance at the wall, thermal resistance of the particles and of the contact area between the particles, thermal resistance of the liquid and gas between particles, the thermal resistance from the particles to the liquid, thermal resistance from the liquid surrounding the particles to the bulk of the gas, and the thermal resistance of both liquid and gas at rest and in motion. In a system such as the guanidine nitrate system, in which gas is generated continuously along the length of the reactor, the effective thermal

conductivity will vary with axial position. A correlation due to Weekman and Myers (Ref. 4) is used to predict the effective thermal conductivity at each axial position and is discussed below.

The second term in the energy balance,  $\rho C_p T / \rho Z$ , accounts for the thermal energy transported by flow in the axial direction. An expression for  $\phi$  is given in Equation (10) as a function of the specific heats of the liquid and gas and the molar flow rates per unit cross-section for the liquid and gas. The third term of Equation (6) describes the contribution to the temperature change due to the change in volume of the melt and gas because of chemical reaction. For this term, the datum temperature was selected for convenience as the feed temperature. An expression for  $\psi$  is given in Equation (11).

The final term of the energy balance is the heat generated by chemical reaction. The heat of reaction and the rate are assumed to be those associated with the guanidine nitrate reaction.

To evaluate the reaction rate expressions for use in the material balance equation, the average radial temperature at each axial position was calculated by Equation (13).

The set of boundary conditions necessary for the solution of these equations is:

1. at  $Z = 0$

$$x_{GN} = x_{GN}^f$$

$$x_U = x_U^f$$

$$x_{AN} = x_{AN}^f$$

$$L = L^f$$

$$G = G^0 = 0$$

$$T(r) = T^f \text{ for all } r$$

where superscript f refers to feed conditions.

2. at  $r = 0$

$$\frac{\partial T}{\partial r} = 0 \text{ for all } Z$$

3. at  $r = r_T$

$$2\pi r_T k_E \left. \frac{\partial T}{\partial r} \right|_{r_T} = -U(T_W - T_f) 2\pi r_{im}$$

for all  $Z$

The presence of the flowing gas phase in the guanidine nitrate system greatly increases the effective thermal conductivity in the packed bed reactor when compared to the effective thermal conductivity that would be expected from the liquid phase alone. The primary effect of the gas is to increase the velocity of the liquid phase. Weekman and Myers (Ref. 4) have proposed and tested the following correlation for predicting the effective thermal conductivity of a packed bed with concurrent gas-liquid flow:

$$\frac{k_E}{k_L} = \frac{7.03}{k_L} + 0.000285 (N_{RE}')_1 (N_{PR})_1$$

where  $(N_{RE}')_1$  is the Reynolds number based on the actual cross-section area available for flow:

$$(N_{RE}')_1 = \frac{D_t L''}{\epsilon R_L}$$

$R_L$  is the fraction of the void volume occupied by the liquid. This definition of Reynolds number follows directly from the liquid mass velocity based on the actual area available for flow of the liquid:

$$L_{ACT}'' = \frac{L''}{\epsilon R_L}$$

Weekman and Myers have tested this correlation for various size spherical packings ranging from 0.149" to 0.255" diameter and over a wide range of

gas and liquid flow rates. They found that this single correlation satisfactorily predicted the thermal behavior of the packed bed. They observed that the amount of heat transferred did not appear to be a function of the tube to particle diameter ratio when this ratio was varied from 11.8 to 20.0. The Reynolds number was therefore based upon the tube diameter. For the Houdry silica beads used in this project, the tube-to-diameter ratio for a 4" column would be approximately 16, which is within the range tested in Ref. 4.

To complete the model,  $R_L$ , the fraction of void volume occupied by the liquid must be predicted at all axial positions. This can be done by utilizing the correlation proposed by Larkins et al. (Ref. 3). In this work, they were able to relate the two-phase friction loss for flow of a liquid and gas through a packed bed to the single phase losses and the fraction of the cross-section occupied by the liquid. For a variety of packings and with gas-liquid systems having a wide range of fluid properties, the following equation was found to apply:

$$\log_{10} R_L = -0.774 + 0.525 (\log_{10} \chi) - 0.109 (\log_{10} f)^2$$

where

$$\chi = \sqrt{S_L / S_g}$$

The terms  $S_L$  and  $S_g$  are the friction losses for the single phase flows of the liquid and gas. These can be predicted by the Ergun equation

(Ref. 1) for pressure drops in packed beds:

$$5 \cdot \left( \frac{g_c \rho D_p^3}{\mu^2} \right) \left( \frac{\epsilon}{1-\epsilon} \right)^3 = N_{Re} (\alpha + \beta N_{Re})$$

where

$$N_{Re} = \frac{D_p L''}{\mu (1-\epsilon)}$$

$$\alpha = 150$$

$$\beta = 1.75$$

The ratio of the liquid to gas phase losses will then equal:

$$\frac{S_L}{S_g} = \frac{N_{ReL} (\alpha + \beta N_{ReL}) \rho_L \mu_L^2}{N_{ReG} (\alpha + \beta N_{ReG}) \rho_G \mu_G^2}$$

#### Numerical Solution

The mathematical model equations were solved on an FMR 6130 digital computer. The ordinary differential equations, Equations (1) through (5), were integrated by utilizing a fourth-order Runge-Kutta routine (Ref. 2). The energy equation however is a partial differential equation and a finite difference method must be used. A Crank-Nicholson 6-point implicit form (Ref. 2) was utilized in generating the solution to the distributed parameter system. This technique was selected over

the singular explicit methods because of its increased accuracy and because of its property of guaranteeing numerically stable solutions.

The step sizes and mode identifications are defined in Figure A-1. In using the Crank-Nicholson method, the temperature derivatives are defined as follows:

$$\frac{\partial T}{\partial z} = \frac{T_{n,s+1} - T_{n,s}}{\Delta z}$$

$$\frac{\partial T}{\partial r} = \frac{1}{4\Delta r} \left[ (T_{n+1,s+1} - T_{n-1,s+1}) + (T_{n+1,s} - T_{n-1,s}) \right]$$

$$\frac{\partial^2 T}{\partial r^2} = \frac{1}{2\Delta r^2} \left[ (T_{n+1,s+1} - 2T_{n,s+1} + T_{n-1,s+1}) + (T_{n+1,s} - 2T_{n,s} + T_{n-1,s}) \right]$$

$$T = \frac{1}{2} (T_{n,s+1} + T_{n,s})$$

When these difference equations are substituted into Equation (6) and the boundary conditions at  $r = 0$  and  $r = r_T$  included, a set of tridiagonal linear equations is obtained of the form:

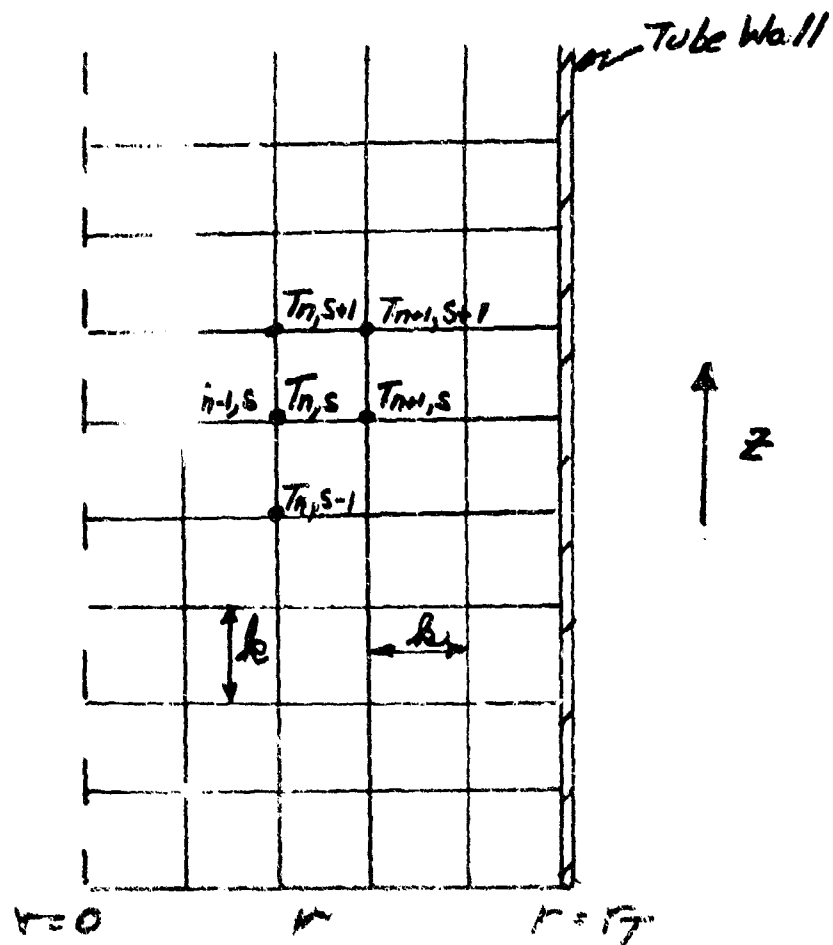


Figure A-1. Description of Nomenclature for Crank-Nicholson Numerical Integration Method



$$C_n \cdot T_{n+1,s+1} + B_n T_{n,s+1} + A_{n-1} T_{n-1,s+1} = D_n$$

where,

$$C_n = \frac{K_E}{2h^2} + \frac{K_E}{4h\tau}$$

$$B_n = \frac{-K_E}{h^2} - \frac{\phi}{k} - \frac{\psi}{2}$$

$$A_{n-1} = \frac{K_E}{2h^2} - \frac{K_E}{4h\tau}$$

$$D_n = -T_{n+1,s} \left\{ \frac{K_E}{2h^2} + \frac{K_E}{4h\tau} \right\} - T_{n,s} \left\{ \frac{-K_E}{h^2} + \frac{\phi}{k} - \frac{\psi}{2} \right\} \\ - T_{n-1,s} \left\{ \frac{K_E}{2h^2} - \frac{K_E}{4h\tau} \right\} + H_R R_{\infty} P_E - \psi \cdot T_1$$

$$\text{for } n=2, N-1$$

and

$$B_1 = -\frac{2K_E}{h^2} - \frac{\phi}{k} - \frac{\psi}{2}$$

$$C_1 = \frac{2K_E}{h^2}$$

$$D_1 = -T_{2,s} \left\{ \frac{2K_E}{h^2} \right\} - T_{1,s} \left\{ \frac{-2K_E}{h^2} + \frac{\phi}{k} - \frac{\psi}{2} \right\}$$

$$+ hR R_{GN} \rho_B - \psi T_1$$

$$B(N) = - \gamma \cdot \left( \frac{KE}{h^2} + \frac{KE}{2h} \right) - \frac{KE}{h^2} - \frac{\phi}{h} - \frac{\psi}{2}$$

$$A(NN-1) = \frac{KE}{h^2}$$

$$D(NN) = - T_{N,s} \left\{ -\frac{KE}{h^2} + \frac{\phi}{h} - \frac{\psi}{2} \right\} - T_{N-1,s} \left\{ \frac{KE}{h^2} \right\}$$

$$+ hR R_{GN} \rho_B - \psi T_1 - \gamma \cdot T_j \left\{ \frac{KE}{h^2} + \frac{KE}{2h} \right\}$$

where

$$\gamma = 2 \text{ h.c. item / unit}$$

This tridiagonal matrix set of equations is solved at each axial position by the Thomas (Ref. 2) algorithm.

SYMBOLS  
FOR  
PACKED BED REACTOR MODEL

- $A$  = cross-sectional area of the reactor, inches<sup>2</sup>
- $C_G$  = specific heat of the gas, calories/(mole)-(<sup>o</sup>K)
- $C_L$  = specific heat of the melt, calories/(mole)-(<sup>o</sup>K)
- $D_t$  = tube diameter, inches
- $D_p$  = diameter of catalyst particle, inches
- $\frac{d(\cdot)}{dZ}$  = first derivative in the axial direction
- $E_i$  = activation energy for component i.
- $G$  = molar flow rate of gas, moles/minute
- $G'$  = molar flow rate of gas based on the empty tube area,  
moles/(inch)<sup>2</sup> - minute.
- $H_R$  = heat of reaction; taken here as the heat of reaction for  
guanidine nitrate production, calories/mole
- $K_E$  = overall effective thermal conductivity, calories/(min)-  
(in)-(<sup>o</sup>K)
- $k_i^o$  = specific rate constant for the formation of component i,  
moles/(gram of catalyst) - (minute)
- $L$  = molar flow rate of melt, moles/minute
- $L'$  = molar flow rate of melt based on the empty tube area,  
moles/(inch)<sup>2</sup> - minute

|                                       |  |
|---------------------------------------|--|
| $N_{PR}$                              | = Prandtl number   |
| $N_{RE}$                              | = Reynolds number  |
| $R_i$                                 | = rate of formation of component i, moles/(gram of catalyst) - (minute)                                      |
| $R_L$                                 | = fraction of the void volume occupied by the melt.  |
| $r$                                   | = radial position, inches  |
| $r_m$                                 | = log mean radius = $(r_{OD} - r_T)/\ln(r_{OD}/r_T)$   |
| $r_{OD}$                              | = outside radius of tube, inches   |
| $r_T$                                 | = radius of the reactor tube, inches   |
| $T$                                   | = temperature, $^{\circ}K$   |
| $T_1$                                 | = reference temperature; taken here as the feed temperature, $^{\circ}K$ .                                   |
| $T_{avg}$                             | = area weighted average radial temperature, $^{\circ}K$  |
| $T_j$                                 | = jacket temperature, $^{\circ}K$  |
| $T_w$                                 | = wall temperature, $^{\circ}K$  |
| $U$                                   | = overall heat transfer coefficient at wall calories/<br>(in <sup>2</sup> ) - (min) - ( $^{\circ}C$ )        |
| $x_i$                                 | = mole fraction of component i.  |
| $z$                                   | = axial position, inches   |
| $\epsilon$                            | = fraction void space in the bed   |
| $\rho$                                | = density  |
| $\rho_B$                              | = bulk packing density of catalyst, grams/cu.in.   |
| $\mu_1$                               | = viscosity of the liquid  |
| $\frac{\partial (\cdot)}{\partial a}$ | = first partial derivative in the a direction  |
| $\psi$                                | = change in melt and gas volume due to chemical reaction - $\frac{\text{cal/min}}{(\text{in}^3)(^{\circ}K)}$ |

## REFERENCES

1. Ergun, S., Chem. Eng. Prog., 48, 89-94 (1952)
2. Lapidus, L., Digital Computation for Chemical Engineers, McGraw-Hill Book Company, Inc., 1962.
3. Larkins, R. P., White, R. R., and D. W. Jeffrey, AIChE Journ., 7, 231 (1961).
4. Weekman, V. W. and J. E. Myers, AIChE Journ., 11, 13 (1965).
5. Terman, G. L., et al., Agr. and Food Chem. 12, 151 (1964)
6. Hauck, R. D., and Stephenson, H. F., Agr. and Food Chem. 12, 147 (1964)
7. Mechalias, B. J., et al., "A Study of Nitrification and Denitrification", Program #17010DRD, Contract #14-12-498, July, 1970. U. S. Govt. Printing Office.
8. Spasskaya, R. I., and Kazarnovskii, S. N., Zh. Prikl. Khim., 35, 1842 (1962), and 34, 3079 (1961).

# Appendix I-2. LISTING OF PROGRAM

## CONTINUOUS PACKED BED REACTOR MODEL

```

C   PACKED BED REACTOR MODEL ---- V. J. COLEMAN
REAL NOIGAS,MOLE110
DIMENSION COEFF1(500)
DIMENSION A( 4, 4),R( 4),C( 4),ANUM( 4),ADEN( 4)
DIMENSION AK(6,4),FUNG(6),YY(6)
DIMENSION Y0( 6),Y( 6),YOLD(6)
DIMENSION CAT(5),KM(6)
DIMENSION WFRAC(6)
DIMENSION YWO(6)
DIMENSION TR1(5),TR2(5)
DIMENSION QPRINT (10)
DIMENSION SAVE(3,50)
COMMON FREQN,FREQD,FCN,EU,BULK,VOID,TEMP,AREA,DIAM,U,TC,PI,
1 HR,CML,CMLC,TD,NOIGAS,OPART,R1,R2,US
KH=2
RETIME KH
NN=51
ND=11
CMR=10.0
CML=45.0
QR=28000.0
PI=3.1416
C   READ IN THE RINGE-KUTTA "ORDER" AND THE COEFFICIENTS.
READ (5,1) M
DO 101 IROW=1,M
READ (5,100) (ANUM(I),I=1,M)
READ (5,100) (ADEN(I),I=1,M)
100 FORMAT (MF10.5)
DO 101 IM=1,M
101 A(IROW,IM)=ANUM(IM)/ADEN(IM)
READ (5,100) (ANUM(I),I=1,M)
READ (5,100) (ADEN(I),I=1,M)
DO 103 IM=1,M
103 B(IM)=ANUM(IM)/ADEN(IM)
READ (5,100) (ANUM(I),I=1,M)
READ (5,100) (ADEN(I),I=1,M)
DO 102 IM=1,M
102 C(IM)=ANUM(IM)/ADEN(IM)
READ (5,1) NCARDS
1   FORMAT (110)
   NC=20 * NCARDS
   READ (5,2) (COMENT(I),I=1,NC)
2   FORMAT (20A4)
   READ (5,6) H,MINT,MTOP,TIME
6   FORMAT (F20.10,2I10,F20.10)
   READ (5,1) N
   READ (5,3) (Y0(I),I=1,N)
3   FORMAT (4F20.10)
   READ (9,2000) (CAT(I),I=1,5),BULK,VOID,OPART
2000 FORMAT (5A5,3F10.5)
   READ (9,2001) DIAM,U,TC,R1,R2,US
2001 FORMAT (8F10.5)
   READ (9,2010) FREQN,FQI,FREQD,FQI

```

```

2010 FORMAT (4F20.10)
      WM(3)=80.0
      WM(4)=60.0
      WM(5)=122.0
      FFE0=Y0(1)
      Y0(1)=Y0(1)+453.6/(Y0(3)*WM(3)+Y0(4)*WM(4)+Y0(5)*WM(5))
      Y0(1)=Y0(1)/60.0
      ANO=Y0(3)*Y0(1)
      DO=Y0(4)*Y0(1)
      GNO=Y0(5)*Y0(1)
      TO=Y0(6)
      TOTAL=0.0
      DO 7010 I=3,5
2010 TOTAL=TOTAL + Y0(I)*WM(I)
      DO 7011 I=3,5
2011 Y0(I)=Y0(I)*WM(I)/TOTAL
      MOL GAS=82.1*(TEMP+273.0)/15.4
      MOL LIQ=3.92
      AREA=PI*DIA**2/4.0
      WRITE (6,31) (CONCENT(I),I=1,NO)
31  FORMAT (1H1,(2Y,20A11))
      WRITE (18,2011) (CAT(I),I=1,5),ROCK,Y0(1)
2011 FORMAT(/1Y,5A4/3Y,10H1K DENSITY =F6.2,10H1K DENSITY =F6.2/3)
1  1VOLE FRACTION =F5.3)
      WRITE (18,2012) DIA
2012 FORMAT (1Y,10H1 DIAMETER =F6.2,10H1 DIAMETER =F6.2)
      TEMP=Y0(6) - 273.0
      WRITE (18,2013) TEMP
2013 FORMAT (1Y,10H1 TEMPERATURE =F6.1,10H1 TEMPERATURE =F6.1)
      WRITE (18,3010) TO,0
3000 FORMAT (1Y,10H1 JACKET TEMPERATURE =F6.1,10H1 JACKET TEMPERATURE =F6.1)
1  1OVERALL HEAT TRANSFER COEFFICIENT =F6.2,10H1 OVERALL HEAT TRANSFER COEFFICIENT =F6.2)
2  )
      TC=TO + 273.0
      WRITE (18,2003)
2003 FORMAT(/1Y,10H1 DISTANCE =F6.2,10H1 DISTANCE =F6.2)
1  1TIME FRACTION =F5.3,10H1 CONVERSION =F5.3,10H1 YIELD =F5.3)
2  1TEMPERATURE =F6.2,10H1 TEMPERATURE =F6.2)
3  1Y,10H1 MOLES/UNIT TIME =F5.3,10H1 MOLES/UNIT TIME =F5.3,10H1 MOLES/UNIT TIME =F5.3)
4  1Y,10H1 D REACT =F5.3,10H1 D REACT =F5.3,10H1 D REACT =F5.3)
5  1Y,10H1 T REACT =F5.3,10H1 T REACT =F5.3,10H1 T REACT =F5.3)
6  1Y,10H1 T REACT =F5.3)
C  REPORT THE CALCULATIONS USING THE INITIAL CONDITIONS.
DO 5 I=1,7
5  Y(I)=Y0(I)
DO 76 I=1,10
10 I(1)=Y(6)
76 T2(I)=T2(I)
1 TOTAL=0
C CONV=0.0
YFEED=1.0
TEMP=Y(5) - 273.0
WRITE (18,2004) TIME,C Y(1),I=1,5),C Y(1),Y(1),I=1,5)

```

```

2004 FORMAT(3F9.3,2Y.5(1X,F9.4),7Y,F7.1)
      ITAPE=0
      NDEF=ND/5
      ITAPE=ITAPE + 1
      WRITE (K0) TIME, (TR2(J),J=1,ND,NDEF)
      RI=1.0
      REIJO=0.0
      WRITE (K0) RI,REIJO
C     BEGIN THE INTEGRATION.
      ICOUNT=0
      DO 15 (TOTAL=1,NTOP
      DO 91 J=1,6
91  YOLD(J)=Y(J)
      CALL RUNGE (X,R,C,Y,TIME,H,AK,FVAL,YY,M,N)
      PK=H
      CALL RADIAL (YOLD,Y,RR,IR1,IR2,PK,RE,REIJO,N)
      TIME=TIME + H
      IF (ITOTAL.EQ. STOP) GO TO 1010
      IF (ITOTAL.LT. 5) GO TO 1010
      ICOUNT=ICOUNT + 1
      IF (ICOUNT.NE. MINT) GO TO 53
      ICOUNT=0
1010 CONTINUE
      CONV=(ND - Y(4)*Y(1))/ND
      YIELD=(Y(5)+Y(1) - GND)/(ND - Y(4)*Y(1))
      TEMP=Y(6) - 273.0
      WRITE (13,2014) TIME,(Y(J),J=1,5),CONV,YIELD,TEMP
      ITAPE=ITAPE + 1
      WRITE (K0) TIME, (TR2(J),J=1,ND,NDEF)
      WRITE (K0) RI,REIJO
5000 FORMAT (1X,IR2 =1,(10F12.4))
      A3 CONTINUE
      DO 80 I=1,N
C     IF (DABS(Y(1)) .LT. 1.0E+60 .AND. DABS(Y(1)) .GT. 1.0E+60)
C     1 GO TO A3
C     WRITE (A,R1)
      R1 FORMAT (7777)
      1*****
      2772X,MAGNITUDE OF Y(1) APPROACHES THE LIMIT OF THE MACHINE,177
      3*****
C     GO TO A2
      A2 CONTINUE
      15 CONTINUE
      WRITE (18,2015) FEEDW,(YND(J),J=3,5)
2015 FORMAT(71X,THE FEED RATE =1,F9.2,11X,749.17
      1 1X,FEED WEIGHT FRACTIONS = 4X40X10X,11X,17.4,
      2 738Y,10X,17.4/25X,10X,17.4/25X,11X,17.4)
      PROD=60.0*Y(1)+(Y(3)*WM(3)+Y(4)*WM(4)+Y(5)*WM(5))/453.6
      TOT=0.0
      DO 2035 I=3,5
      WRA(I)=Y(I)*P(I)
2035 TOT=TOT + WRA(I)
      DO 2040 I=3,5

```



```

2040 EFAC(I)=EFAC(I)/TOT
      WRITE (14,2036) FPOB,(EFAC(I),I=3,5)
2046 FORMAT (1Y,1P,PRODUCT RATE =1F7.3,1 (R,20,1/1Y,1P,UNIT WEIGHT FRAC-
TIONS = 1 AMMONIUM NITRATE =1F7.4/41X,100FA =1F7.4/
2 2SX,1GUANIDINE NITRATE =1F7.4)
      CAT=AREA*HOLD*TIME
      WRITE (18,2016) CAT
2016 FORMAT(1X,1TOTAL CATALYST WEIGHT =1,F8.2,1 (CAT(S))
      RTIME=AREA*TIME/(VO(1)*SCILLIC)
      WRITE (18,2017) RTIME
2017 FORMAT(1X,1NOMINAL RESIDENCE TIME =1,F7.2,1 (MINUTES)
C      WRITE (18,2018) MOLD GAS,LIQ LIQ
2018 FORMAT(1X,1MOLAR VOLUME OF GAS =1F9.2,1 (CU. IN./G.-MOLE/1X,1MOLAR
VOLUME OF LIQUID =1,F6.2,1 (CU. IN./G.-MOLE)
C      WRITE (18,2019) H
2019 FORMAT(1X,1INTEGRATION STEP SIZE =1,F5.2)
      WRITE (18,2020) FREQG,FGK,FREQD,ED
2020 FORMAT(1X,1RATE CONSTANT FOR G- 1/5X,1FREQUENCY FACTOR =1E12,4/5X
1,1ACTIVATION ENERGY =1E12,4/1X,1RATE CONSTANT FOR DREA DECOMPOSITI
ION/5X, 1FREQUENCY FACTOR =1E12,4/5X,1ACTIVATION ENERGY =1E12,4)
      PH=R/5,0
      DO 74 J=1,6
74 RPRINT(J)=PH+FI*CAT(J-1)
      WRITE (14,75) (RPRINT(J),J=1,6)
75 FORMAT (1H1,7/1X,1DISTANCE1,2SX,1RADIAL TEMPERATURE FROM
11E5/1X, 6(3X,1R =1F7.3,2X)1)
      REWIND KU
      DO 77 I=1,11APF
      READ (50) TIME,(TR2(I),I=1,10,NREF)
      READ (50) RI,REF10
      SAVE(1,1)=TIME
      SAVE(2,1)=RI
      SAVE(3,1)=REF10
      DO 79 I=1,NN,NREF
79 TR2(I)=TR2(I) - 273.0
77 WRITE (14,78) TIME,(TR2(I),I=1,10,NREF)
78 FORMAT (10,3,6(F12.3,4X))
      WRITE (14,95)
95 FORMAT (1H1,16Y,1TIME1,1RX,1RI1,15X,1REF101/2)
      DO 96 I=1,11APF
96 WRITE (14,97) (SAVE(I,1),J=1,3)
97 FORMAT (3F20,4)
82 CONTINUE
      END

```



```

SUBROUTINE ROUNG (A,Z,C,N,TIME,PAK,P,CO,YI,PI)

```

```

C
C *****
C THIS SUBROUTINE INTEGRATES A SET OF ORDINARY DIFFERENTIAL EQUATIONS
C OVER ONE STEP BY A GENERALIZED EXPLICIT RUNGE-KUTTA ALGORITHM.
C THE RUNGE-KUTTA COEFFICIENTS MUST BE PROVIDED AS ARGUMENTS.
C FOR EVALUATING THE SYSTEM EQUATIONS.
C CHARGES SHOULD BE PROVIDED IN THE OTHER ARGUMENTS.
C *****

```

```

C FOR A SINGLE PRECISION VERSION OF THIS PROGRAM, REMOVE THE FOLLOWING
C PARTS.

```

```

IMPLICIT REAL*8 (A-H,O-Z)

```

```

C*****

```

```

DIMENSION A(N,M),B(M),C(M),Y(M),AK(M,M),F(10),X(M)

```

```

C
C CONECLATURE

```

```

C M = NUMBER OF FUNCTION EVALUATIONS IN THE RUNGE-KUTTA ALGORITHM.

```

```

C A = ARRAY OF DIMENSION (M X N).

```

```

C B = VECTOR OF DIMENSION M.

```

```

C C = VECTOR OF DIMENSION M.

```

```

C N = NUMBER OF SYSTEM EQUATIONS TO BE INTEGRATED.

```

```

C X = VECTOR OF DIMENSION N OF INDEPENDENT VARIABLES.

```

```

C H = INTEGRATION STEP SIZE.

```

```

C TIME = INDEPENDENT VARIABLE.

```

```

C
C GENERALIZED RUNGE-KUTTA REPRESENTATION

```

```

C
C      F(1) = A(1,1)  A(1,2)  . . . . . A(1,N)
C      F(2) = A(2,1)  . . . . . A(2,N)
C      . . . . .
C      . . . . .
C      . . . . .
C      F(10) = A(10,1) . . . . . A(10,N)
C
C      -----
C      F(8) = B(1)  B(2) . . . . . B(N)

```

```

C
C      F(2) = A(2,1)  . . . . . A(2,N)
C
C      . . . . .
C
C      . . . . .
C
C      F(10) = A(10,1) . . . . . A(10,N)

```

```

C
C      -----
C
C      F(8) = B(1)  B(2) . . . . . B(N)

```

```

C
C      F(2) = A(2,1)  . . . . . A(2,N)
C
C      . . . . .
C
C      . . . . .
C
C      F(10) = A(10,1) . . . . . A(10,N)

```

```

C
C      -----
C
C      F(8) = B(1)  B(2) . . . . . B(N)

```

```

C
C      F(2) = A(2,1)  . . . . . A(2,N)
C
C      . . . . .
C
C      . . . . .
C
C      F(10) = A(10,1) . . . . . A(10,N)

```

```

C
C      -----
C
C      F(8) = B(1)  B(2) . . . . . B(N)

```

```

C
C      F(2) = A(2,1)  . . . . . A(2,N)
C
C      . . . . .
C
C      . . . . .
C
C      F(10) = A(10,1) . . . . . A(10,N)

```

```

C
C      -----
C
C      F(8) = B(1)  B(2) . . . . . B(N)

```

```

C
C      F(2) = A(2,1)  . . . . . A(2,N)
C
C      . . . . .
C
C      . . . . .
C
C      F(10) = A(10,1) . . . . . A(10,N)

```

```

C
C      -----
C
C      F(8) = B(1)  B(2) . . . . . B(N)

```

```

C
C      F(2) = A(2,1)  . . . . . A(2,N)
C
C      . . . . .
C
C      . . . . .
C
C      F(10) = A(10,1) . . . . . A(10,N)

```

```

C
C      -----
C
C      F(8) = B(1)  B(2) . . . . . B(N)

```

```

C
C      F(2) = A(2,1)  . . . . . A(2,N)
C
C      . . . . .
C
C      . . . . .
C
C      F(10) = A(10,1) . . . . . A(10,N)

```

```

C
C      -----
C
C      F(8) = B(1)  B(2) . . . . . B(N)

```

```

C
C      F(2) = A(2,1)  . . . . . A(2,N)
C
C      . . . . .
C
C      . . . . .
C
C      F(10) = A(10,1) . . . . . A(10,N)

```

```

C
C      -----
C
C      F(8) = B(1)  B(2) . . . . . B(N)

```

```

C
C      F(2) = A(2,1)  . . . . . A(2,N)
C
C      . . . . .
C
C      . . . . .
C
C      F(10) = A(10,1) . . . . . A(10,N)

```

```

C
C      -----
C
C      F(8) = B(1)  B(2) . . . . . B(N)

```

```

C
C      F(2) = A(2,1)  . . . . . A(2,N)
C
C      . . . . .
C
C      . . . . .
C
C      F(10) = A(10,1) . . . . . A(10,N)

```

```

C
C      -----
C
C      F(8) = B(1)  B(2) . . . . . B(N)

```

```

C
C      F(2) = A(2,1)  . . . . . A(2,N)
C
C      . . . . .
C
C      . . . . .
C
C      F(10) = A(10,1) . . . . . A(10,N)

```

```

C
C      -----
C
C      F(8) = B(1)  B(2) . . . . . B(N)

```

```

C      EVALUATE THE SYSTEM EQUATIONS.
      XX=TIME + C(IN)*H
      CALL SYSTEM(XX,YY,FUNC,I)

C
      DO 3 I=1,N
3      AK(IN,I)=R + FUNC(I)
4      CONTINUE

C
C      CALCULATE THE PRODUCT OF THE X'S AND Y'S.
      DO 5 I=1,N
      DOTPRD=0.0
      DO 6 J=1,M
6      DOTPRD=AK(IN,I) * R(J) + DOTPRD
5      Y(IN)=Y(IN) + DOTPRD

C
      RETURN
      END

```

```

SUBROUTINE PARTIAL (Y,XY,XP,T01,T02,PK,PI,0110,0111)
REAL MOLFAS,MOLLE
DIMENSION Y(6),X(6),AA(6),PR(6),L(6),D(6),D1(6),D2(6)
DIMENSION XAY(6)
COMMON FREQ01,FREQ02,F0,F01,RI,K,V010,TF,TA,AF,AL,AM,DT,PI,
1 MS,ME,PM,TD,SOLFAS,PPART,X1,X2,TS
DATA ALPHA,BETA,VIS1,VIS2,KPOL,CP/15.0,1.75,1.0,0.02,1.0,0.50/
DO 2 I=1,6
2 T01(I)=T02(I)
C EQUATION EQUATIONS
VIS1=VIS1*2.54*0.5
VIS2=VIS2*2.54*0.5
R000=25.0/(MOLFAS*16.4)
G11=Y(1)*(Y(3)*X(3)+Y(4)*X(4)+Y(5)*X(5))/A*2
GRAS=Y(2)*2K*P/AF*PA
REF10=PPART*G11/(VIS1*(1.0-V010))
REFAS=PPART*GRAS/(VIS2*(1.0-V010))
REF10=REF10*(ALPHA+BETA*REF10)*R000*(1.0**2
REFAS=REFAS*(ALPHA+BETA*REFAS)*R000*(V15**2
C FURTHER EQUATIONS
IF (REFAS-1.0-1.0E-05) GO TO 20
CHI=SQRT(REF10/REFAS)
IF (CHI-1.0-1.0E-05) GO TO 5
20 SI=1.0
GO TO 4
4 SI=-.774+0.525*AL*CHI*(CHI-0.10)*(.AL*SI*(2.0-1.0)**2
SI=0.0**SI
5 CONTINUE
C FURTHER
REFAS=AL*G11/(VIS1*V010*SI)
R000=1.0
AF=VIS1*2.42
PPART=PP*AP*H/CO*AT
EFK=7.03+2.85E-04*(1.0+2.0*Y(1)*P*10
EFK=EFK*0.1*AF*E-03+2.03*0.0
C THERMAL ANALYSIS SYSTEM
X00=REF10*GRAS*Y01*(-G1/Y(1))
S00=REF10*GRAS*Y02*(-G2/Y(2))
G1=SP*Y(4)*Y(3)
G2=SP*Y(3)*Y(4)**2
L1=D0*RI*K
L2=5.0*K*G0*2*01K
D01=(D1*Y(1)+D2*Y(2))/AF*PA
D02=ME*F1+D*PK*F2
G0S=D0*200*P01*-D01*TD
P0=RI/ZE/DAT(X-1)
AT=NN*1
DO 10 I=2,61
2AN=D0*F1/DAT(I-1)
D01(I)=EFK/(2.0*D0**2)+EF1/(0.0*D0**2.0)
D0(I)=EFK/D0**2+D01/D0-D01/2.0
AA(I-1)=EFK/(2.0*D0**2)-EFK/(0.0*D0**2.0)
C=D0(I)

```

```

R=EEFK/(PH**2)+PHI/PK-PSI/2.0
A=AA(J-1)
10 DD(J)=-TR1(J+1)*C-TR1(J)*R-TR1(J-1)*A+RHS
RR(1)=2.0*EEFK/PH**2-PHI/PK-PSI/2.0
CC(1)=2.0*EEFK/PH**2
C=CC(1)
R=2.0*EEFK/PH**2+PHI/PK-PSI/2.0
DD(1)=-TR1(2)*C-TR1(1)*R+RHS
RAT=PH*FLOAT(IN=1)
RLNM=(R2-R1)/ALOG(R2/R1)
TERM=2.0*PH*US*RLNM/(EEFK*QAD)
RR(NN)=EEFK/PH**2-PHI/PK-PSI/2.0-2.0*TERM*(EEFK/(2.0*PH**2)
1+EEFK/(4.0*PH*QAD))
AA(NN=1)=EEFK/PH**2
DD(NN)=-TR1(NN)*(-EEFK/PH**2+PHI/PK-PSI/2.0)
1 -TR1(NN-1)*(EEFK/PH**2) + RHS
2=2.0*TERM*TC*(EEFK/(2.0*PH**2) + EFK/(4.0*PH*QAD))
CALL TRIDAG(AA,RR,CC,DD,NN)
DO 11 I=1,NN
11 TR2(J)=DD(J)
SUM=0.0
DO 15 I=2,NN
TAV=(TR2(J)+TR2(I-1))/2.0
RAT1=PH*FLOAT(I-2)
RAT2=PH*FLOAT(I-1)
15 SUM=SUM+TAV*FI*(RAT2**2-RAT1**2)
XXX(6)=SUM/(PI*RAT2**2)
RETURN
END

```

```

SUBROUTINE TRIDAG (A,B,C,D,N)
DIMENSION A(N),B(N),C(N),D(N)
P(1)=D(1)/B(1)
Q=0
DO 1 J=2,N
  P(J-1)=C(J-1)/B(J-1)
  Q=0
  DO 2 I=J-1,1
    P(I)=(C(I)-A(I-1)*P(I-1))/B(I)
    Q=0
  2  D(I)=D(I)-A(I-1)*P(I-1)
  1  P(I)=(D(I)-A(I-1)*P(I-1))/B(I)
  Q=Q+C(I)*P(I)
  1  D(I)=D(I)-A(I-1)*P(I-1)
  2  D(I)=D(I)-A(I-1)*P(I-1)
RETURN
END

```

## APPENDIX I-3

### CONTINUOUS STIRRED TANK MODEL

A detailed description of the continuous stirred tank model is presented in this section. The method of solution of the discrete difference equations is also given.

#### Model Development

Consider the series of stirred tanks depicted in Figure B-1. The material balances for guanidine nitrate, urea, and ammonium nitrate can be written for the nth tank:

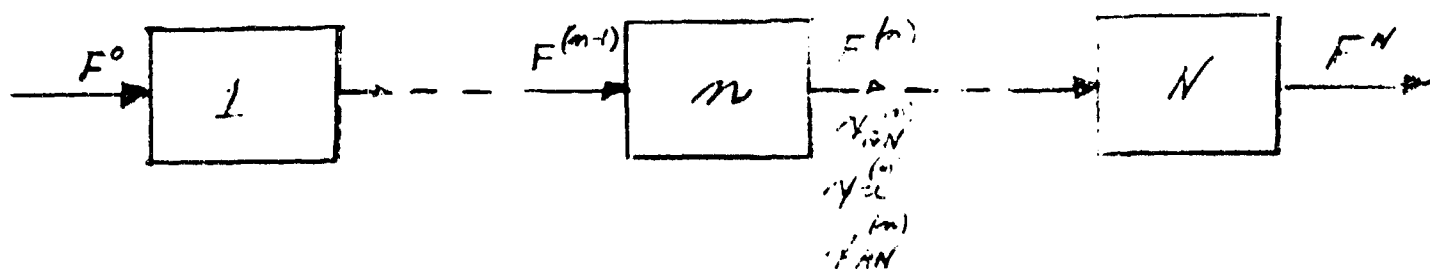
$$\begin{aligned} (1) \quad F^{(n)}_{\text{Guan}} &= F^{(n-1)}_{\text{Guan}} + R_{\text{Guan}} \cdot \Delta t \\ (2) \quad F^{(n)}_{\text{Urea}} &= F^{(n-1)}_{\text{Urea}} + R_{\text{Urea}} \cdot \Delta t \\ (3) \quad F^{(n)}_{\text{NaN}} &= F^{(n-1)}_{\text{NaN}} + R_{\text{NaN}} \cdot \Delta t \end{aligned}$$

The notation is defined at the end of this section. Notice that both sides of each equation have been divided by the molar feed rate to the first vessel,  $F^0$ , so that the factors  $F^{(n)}$ ,  $F^{(n-1)}$ , and  $W_C^{(n)}$  are all expressed on the same basis of one mole/minute of feed to the first reactor. The rate expressions are given by:



FIGURE B-1

CASCADE OF  $N$  STIRRED TANKS



$W_c^{(n)}$  - grams of catalyst in reactor  $n$ .

$$\begin{aligned}
 (4) \quad R_{AN}^{(n)} &= K_u^{(n)} \cdot N_{AN}^{(n)} \cdot k_{AN}^0 e^{-E_{AN}/R \cdot T^{(n)}} \\
 (5) \quad R_{u}^{(n)} &= -K_u^{(n)2} \cdot N_{AN} \cdot k_u^0 e^{-E_u/R T^{(n)}} \\
 (6) \quad R_{AN}^{(n)} &= -R_{u}^{(n)}
 \end{aligned}$$

By summing Equations (1), (2), and (3), the following equation relating the flow rates results:

$$(7) \quad F^{(n)} = F^{(n-1)} + R_u^{(n)} \cdot W_c^{(n)}$$

Equations (1) through (7) are solved simultaneously for each tank in sequence.

#### Numerical Solution

If Equations (5) and (7) are substituted into Equation (2), the following cubic equation results:

$$(1) \left(x_u^{(n)}\right)^3 - \left(x_u^{(n)}\right)^2 - M x_u^{(n)} + 1/x_u^{(n-1)} = 0$$

where

$$M = \frac{f^{(n-1)}}{h_u^{(n)} \cdot h_{AN}^{(n)}}$$

$$h_u^{(n)} = h_u^0 e^{-E_u/RT^{(n)}}$$

All terms with superscript (n-1) are known and those terms with superscript (n) are unknown. Therefore, before Equation (8) can be solved for  $x_u^{(n)}$ , an Equation for  $x_{AN}^{(n)}$  must be provided in order that M can be specified. By substituting Equations (6) and (4) into Equation (3), the following quadratic expression results:

$$(2) \left(x_{AN}^{(n)}\right)^2 - N x_{AN}^{(n)} + P x_{AN}^{(n-1)} = 0$$

where

$$N = \frac{w_c^{(n)} \cdot k_{AN}^{(n)} \cdot x_u^{(n)} + F^{n-1}}{w_c^{(n)} k_{AN}^{(n)} (f_u^{(n)})^2}$$

$$P = \frac{F^{n-1}}{w_c^{(n)} k_{AN}^{(n)} (f_u^{(n)})^2}$$

$$k_{AN} = k_{AN}^0 e^{-E_{AN}/RT}$$

Equations (8) and (9) are simultaneous functions of the unknown  $x_{AN}^{(n)}$  and  $x_u^{(n)}$ . These equations for the nth reactor were solved by the following iterative algorithm:

1. Assume a value for  $x_{AN}^{(n)}$ . A convenient first assumption is  $x_{AN}^{(n)} = x_{AN}^{(n-1)}$
2. Solve the cubic equation, Equation (8), for  $x_u^{(n)}$
3. Using this value for  $x_u^{(n)}$ , solve the quadratic equation, Equation (9), for  $x_{AN}^{(n)}$

4. Check whether this value of  $x_{AN}^{(n)}$  is equal to that assumed in step 1. If it is, the solution for  $x_{AN}^{(n)}$  and  $x_u^{(n)}$  for the nth reactor is complete. If not, repeat this procedure from step 2 using this newly generated value of  $x_{AN}^{(n)}$ .

Using this procedure, no convergence difficulties were encountered for any of the cases treated. A listing of the computer program for solving the stirred tank model is included in Appendix I-4.

SYMBOLS  
FOR  
STIRRED TANK REACTOR MODEL

$E_i$  = activation energy for component  $i$ .

$F^{(n)}$  = molar flow rate of stream  $(n)$  per mole/minute of feed

$k_i^o$  = specific rate constant for the formation of component  $i$ , moles/(gram of catalyst)-(minute)

$R_i^{(n)}$  = rate of formation of component  $i$  in reactor  $(n)$ ;  
moles/(gram of catalyst)-(minute)

$W_c^{(n)}$  = weight of catalyst in reactor  $(n)$

$x_i^{(n)}$  = mole fraction of component  $i$  in stream  $(n)$ .

## APPENDIX I-4. LISTING OF PROGRAM

## CONTINUOUS STIRRED TANK REACTOR MODEL

```

10  CONTINUE DO 10 STIRRED TANK REACTOR MODEL -- 1.0, 0.0, 0.0
20  OPENING CONVERT(40),CAT(5),TEMP(5),C(1),CAT(1),Z(5),Z(5),
30  Y=0(5),X(5),YFEED(5),XFEED(5),X(5),Y(5)
40  PRT(1)=0.75
50  RETPOV=0.5
60  READ(0,1)NTA=KS
70  READ(0,3)(WCAT(1),I=1,NTA)KS
80  READ(0,1)(ND=999) NTAKS
90  Z(1)=1/ANTS
100 READ(0,2)(CONCENT(1),I=1,20)
110 READ(0,2000)(CAT(1),I=1,5),BULK,POROSITY
120 READ(0,3)(TEMP(1),I=1,NTA)KS
130 READ(0,2010)F=9.0,C=1.0,FEED=0,FD
140 READ(0,3)(END=999) (X(1),I=1,3),YFEED
150 1 FORMAT(8F10)
160 2 FORMAT(20A4)
170 3 FORMAT(4F20,10)
180 2010 FORMAT(5A4,3F10,5)
190 2010 FORMAT(4F20,10)
200 5 I=1,NTA=KS
210 VOL(1)=WCAT(1)*2.0/((0.01+1728.0)
220 C(1)=50.0
230 C(2)=50.0
240 C(3)=122.0
250 TOTAL=0.0
260 5 I=1,3
270 TOTAL=TOTAL+X(1)*C(1)
280 7 I=1,3
290 Y(1)=Y(1)*Z(1)/TOTAL
300 FEED=FEED+TOTAL*(7.0/2500.0)
310 Y(4)=FEEDW
320 X(4)=FEEDW
330 WRITE(15,31)(CONCENT(1),I=1,20)
340 31 FORMAT(10F10,2X,(20A4))
350 31 WRITE(15,2011)(CAT(1),I=1,5),BULK,POROSITY
360 2011 FORMAT(/1X,5A4/3X,16F10,1)TEMP=TEMP(1),Z(5),Z(5),C(1),
370 1 POROSITY=10.0,Z(1),VOL(201,1)
380 31 WRITE(15,2011)
390 2010 FORMAT(1X,10F10,1)TOTAL=TOTAL+X(1)*C(1)+X(4)*C(4)
400 15 AND PRODUCT FLOW RATES AND GIVENS Z(5),CAT(5),TEMP(5),FEED=0,
410 2 FEED=CAT(1) FOR FIRST REACTION,1)
420 5 I=1,4
430 YFEED(1)=Y(1)
440 50 I=1,NTA=KS
450 WCAT=WCAT(5)*7.48/((0.01+1728.0)
460 VOLGAL=VOL(5)*7.48
470 21 WRITE(15,5000)WCAT(5),VOLGAL,TEMP(5),C(5),VOLGAL
480 5000 FORMAT (/1X,1REACTOR,12,5X,1CATALYST=1,10,2,1,1C(5),1,
490 1 10,4,1,CAT,1Z1X,1TEMPERATURE=1,5,1,1,1Z1X,
500 2 1NONREACT VOLUME=1,10,2,1,1C(1),1,1C(1),1C(1),1C(1),1Z)
510 21 WRITE(15,5001)C(5001),X(1),Y(1),I=1,3)
520 5001 FORMAT(10Y,1F10,FEED=1,10,2,1,1C(1),1Z,1,1Z,
530 1 11,10,1REACT=1,10,2,1,1C(1),1C(1),1C(1),1C(1),1Z,4Z

```

```

252Y, IGUANIDINE NITRATE =1F7.4)
WRITE(18,5002) X0(4), (XP(1), I=1,3)
5002 FORMAT(10X, 'FEED FLOW RATE =1F7.4, ' / 13, 'ZNF, ' / 14X,
1 MOLE FRACTIONS / 53X, 'AMMONIUM NITRATE =1F7.4 / 53X, 'UREA =1F7.4 /
252Y, IGUANIDINE NITRATE =1F7.4)
SPGN=FEQGN*EXP(-EGN/(TEMP(K)+273.0))
SPU=FEQU*EXP(-EU/(TEMP(K)+273.0))
ICOUNT=0
XU=-1.0
XAN=X0(1)
53 ICOUNT=ICOUNT+1
A=1.0
B=-1.0
C=X0(4)/(WCAT(K)+SPU*XAN)
D=C*X0(2)
CALL CPBIC(A,B,C,D,XX,XTE(2),ITYPE,NREAL)
A=0.0
R=WCAT(K)+SPU*XTE(2)**2
C=-WCAT(K)+SPGN*XTE(2)-X0(4)
D=X0(4)*X0(1)
CALL CPBIC(A,B,C,D,XX,XTE(1),ITYPE,NREAL)
IF(ABS((XTE(1)-XAN)/XAN),GT,1.0E-05) GO TO 51
IF(ABS((XTE(2)-XU)/XU),GT,1.0E-05) GO TO 51
GO TO 52
51 XU=XTE(2)
XAN=XTE(1)
IF(ICOUNT,LT,50) GO TO 53
WRITE(18,54)XU,XTE(2),XAN,XTE(1)
54 FORMAT(// 'ITERATION IS NOT CONVERGE SIZE 12.1)
CALL EXIT
52 XTE(4)=X0(4)-WCAT(K)+SPU*XTE(1)*XTE(2)**2
XTE(3)=(1.0/XTE(4))*(X0(4)*X0(3)+WCAT(K)+SPU*XTE(1)*XTE(2))
CONV=(XTE(2)*XTE(4)-XTE(2)*XTE(4))/(XTE(2)*XTE(4))
CONV=-CONV
YIELD=(XTE(3)*XTE(4)-XTE(3)*XTE(4))/
1 (XTE(2)*XTE(4)-XTE(2)*XTE(4))
YIELD=-YIELD
GAS=3.0*WCAT(K)+SPGN*XTE(1)*XTE(2)
TOTAL=0.0
DO 9 I=1,3
9 TOTAL=TOTAL+XTE(I)*WM(I)
DO 10 I=1,3
10 XWTE(I)=XTE(I)*WM(I)/TOTAL
XWTE(4)=XTE(4)*(60.0/453.6)/TOTAL
WRITE(18,5003)XWTE(4), (XWTE(I), I=1,3)
5003 FORMAT(10X, 'PRODUCT FLOW RATE =1F7.4, ' / 13, 'ZNF, ' / 14X,
1 WEIGHT FRACTIONS / 53X, 'AMMONIUM NITRATE =1F7.4 / 53X, 'UREA =1F7.4 /
252Y, IGUANIDINE NITRATE =1F7.4)
WRITE(18,5004)XTE(4), (XTE(I), I=1,3)
5004 FORMAT(10X, 'PRODUCT FLOW RATE =1F7.4, ' / 13, 'ZNF, ' / 14X,
1 MOLE FRACTIONS / 53X, 'AMMONIUM NITRATE =1F7.4 / 53X, 'UREA =1F7.4 /
252Y, IGUANIDINE NITRATE =1F7.4)
WRITE(18,5005) GAS

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```

5005 FORMAT(10X,'GAS FLOW RATE =',F7.4,' MOLES/MINUTE')
      WRITE(18,5005) (CONV, YTF(I))
5006 FORMAT(10X,'TOTAL CONVERSION =',F7.4,' MOLES PER PERCENT OF AREA
      1 PERCENT/10X,' TOTAL YIELD =',F7.4,' MOLES PERCENT PERCENT OF AREA
      1 PERCENT')
      WRITE(18,2020) (FREQ, FREQ, FREQ, FREQ)
2020 FORMAT(10X,'RATE CONSTANT FOR G1/15X, PERCENT FACTOR =',F12.4,
      1 15X,'ACTIVATION ENERGY =',F12.4/10X,' AT 20 STATE FOR AREA PERCENT
      2 STATE/15X, PERCENT FACTOR =',F12.4/15X,'ACTIVATION ENERGY =',
      3  F12.4)
      DO 11 I=1,4
      Y2D(I)=YTF(I)
11  Y0(I)=YTF(I)
      WRITE(18,311) (CONV(I), I=1,4)
      50 CONTINUE
      GO TO 908
999 CALL EXIT
      END

```

```

SUBROUTINE CURTIC(A,B,C,D,XY,XREAL,ITYPE,XREAL)
C SOLUTION OF CURTIC AND QUADRATIC EQUATIONS.
DIMENSION YX(3),IROUND(3)
CURRT(ARG)=SIGN(ABS(ARG)**(1.0/3.0),ARG)
DO 500 I=1,3
500  IROUND(I)=0
      IF(A)200,110,200
110  IF(B)140,120,140
120  IF(C)130,999,130
130  X=-D/I
      XY(1)=X
      ITYPE=1
      GO TO 100
140  P=-C/(B+I)
      Q=-D/I
      R=P+P+Q
      IF(R)160,150,150
150  Y=SIGN(ABS(P)+SORT(P),P)
      Y=-Q/Y
      XY(1)=Y
      XY(2)=Y
      ITYPE=2
      GO TO 100
160  Y=SIGN(ABS(P)+SORT(P),P)
      XY(1)=0.0
      XY(2)=P
      XY(3)=Y
      ITYPE=3
      GO TO 100
200  IF(D)300,210,300
210  X=0.0
      IF(E)230,220,230
220  X2=0.0
      Y1=-B/A
      GO TO 330
230  P=-B/(A+I)
      Q=-C/A
      R=P+P+Q
      IF(R)250,240,240
240  Y1=P+SIGN(P)
      X2=P+P-X1
      GO TO 330
250  Y=SIGN(ABS(P)+SORT(P),P)
      GO TO 350
300  P=B/(3.0+A)
      Q=C/(3.0+A)
      R=Q/A
      ALPHA=Q+P+P
      BETA=ALPHA+P+0.5*(P+Q-R)
      GAMMA=ALPHA+ALPHA+ALPHA+BETA+0.5*A
      IF (GAMMA.GT.1.E-5) GO TO 340
      IF (GAMMA.GT.-1.E-5) GO TO 320
310  SORT=SIGN(1-GAMMA)

```



```

      CALL EXIT
503 GO TO (601,602,603),ICOUNT
504 DO 505 I=1,NREAL
      IF (ICOUNT(I).NE.1) GO TO 605
      XREAL=XX(I)
505 CONTINUE
      RETURN
506 WRITE (14,506) (XX(I),I=1,3)
506 FORMAT (//,'TWO REAL ROOTS BETWEEN 0 AND 1',3E12.4)
      CALL EXIT
507 WRITE (14,507) (XX(I),I=1,3)
507 FORMAT (//,'THREE REAL ROOTS BETWEEN 0 AND 1',3E12.4)
      CALL EXIT
      END
      EOF

```

# APPENDIX I-5. COST STUDIES

001 STUDY - GUANIDINE NITRATE  
CODE NO.101

Basic Case

Basis: Cont. Process; 1 hr. reaction

AN/U/Cat. = 2/2/1.7

U Yld. = 80%; U Conv. = 64.5%

AN Yld. = 100%; AN Conv. = 32%

\* PRODUCTION COSTS

| PLANT CAPACITY             | 80.0 TON/LB/HR | 80.0 TON/LB/HR | 80.0 TON/LB/HR | 80.0 TON/LB/HR | Gov't<br>Acctg |
|----------------------------|----------------|----------------|----------------|----------------|----------------|
|                            | UNITS          | DATE/HR        | LI             | ELY            | CHANGE         |
| INVESTMENT (MM \$)         |                |                |                |                |                |
| BATTERY LIMIT              |                |                |                | 1.40           | 6.42           |
| OFFSITE AND ALLOCATED AUX. |                |                |                | 1.20           | 1.20           |
| TOTAL (MM \$)              |                |                |                | 7.62           | 7.62           |

## PROCESSING COST (CENTS/LB)

|                  |              |             |           |      |      |
|------------------|--------------|-------------|-----------|------|------|
| DEPRECIATION     |              | 10.0 PCT/HR |           | .95  | -    |
| EX. AND RL       |              | 5.0 PCT/HR  |           | .72  | .24  |
| OPERATING LABOR  | 16.00 HRN    | 8600.0      | 8.700-1.7 | .17  | .17  |
| CHEMICAL CONTROL | 4.00 HRN     | 10000.0     | 1.700-1.7 | .05  | .05  |
| SUPERVISION      | 4.00 HRN     | 12000.0     | 1.700-1.7 | .06  | .05  |
| ELECTRICITY      | .20 KWH/LB   | 1.0         | 0.125-1.7 | .04  | .20  |
| STEAM            | 4.00 LB/LB   | 75.0        | 0.125-1.7 | .04  | .30  |
| WATER            | 10.00 GAL/LB | 10.0        | 0.125-1.7 | .10  | .10  |
| FUEL             | .01 GAL/LB   | 7.0         | 0.125-1.7 | .10  | .10  |
| TOTAL (CENTS/LB) |              |             |           | 0.99 | 1.22 |

## RAW MATERIAL COST (CENTS/LB)

|                  |               |        |           |      |      |
|------------------|---------------|--------|-----------|------|------|
| UREA             | 1.23200 LB/LB | 7.00   | 0.125-1.7 | 1.93 | 4.93 |
| AMMONIUM NITRATE | .65600 LB/LB  | 0.65   | 0.125-1.7 | 1.64 | 1.64 |
| CATALYST         | .00100 LB/LB  | 150.00 | 0.125-1.7 | .15  | .15  |
| TOTAL (CENTS/LB) |               |        |           | 6.72 | 6.72 |

## PLANT OVERHEAD (CENTS/LB)

|  |  |  |  |      |     |
|--|--|--|--|------|-----|
| TOTAL MILL COST (CENTS/LB) EX. BY-PRODUCT CREDIT |  |  |  | 0.31 | .18 |
|--|--|--|--|------|-----|

## BY-PRODUCT CREDIT (CENTS/LB)

|                    |              |     |           |     |      |
|--------------------|--------------|-----|-----------|-----|------|
| AMMONIUM CARBAMATE | .60000 LB/LB | .00 | 0.125-1.7 | .00 | .000 |
| TOTAL (CENTS/LB)   |              |     |           | .00 | .00  |

|   |  |  |  |      |      |
|---|--|--|--|------|------|
| TOTAL MILL COST (CENTS/LB) INC. BY-PRODUCT CREDIT |  |  |  | 0.31 | 8.12 |
|---|--|--|--|------|------|

Fringe 1.69

Price 0% Return 9.81¢/lb

\* 10 YEAR PLANT LIFE, EXISTING SITE  
15 PCT INDIRECT

\*\* PERCENT CHANGE NEEDED TO AFFECT RETURN BY 5 PERCENTAGE POINTS

## OTHER CALCULATIONS

(1) 50% is maintenance material

|                  |         |
|------------------|---------|
| PLANT INVESTMENT | \$ 7.62 |
| OFFSITE ALLOC.   | \$ 1.20 |
| TOTAL INVESTMENT | \$ 8.82 |
| TOTAL COSTS      | \$ 9.00 |

|                            |               |
|----------------------------|---------------|
| PRICE FOR 10 YR PLANT LIFE | 11.0 CENTS/LB |
| PRICE FOR 20 YR PLANT LIFE | 10.0 CENTS/LB |
| PRICE FOR 30 YR PLANT LIFE | 12.0 CENTS/LB |

COST STUDY - GUANIDINE NITRATE  
CASE NO.102

Basis: Cont. Process; 1 hr. reaction  
AN/U/Cat. = 2/2/1.7  
U Yld. = 80%; U Conv. = 64.5%  
AN Yld. = 100%; AN Conv. = 32%

\*PRODUCTION COSTS

| PLANT CAPACITY             | 20.0 MM LB/YR |           |        | ***SENSITIVITY |             |
|----------------------------|---------------|-----------|--------|----------------|-------------|
|                            | UNITS         | RATE/UNIT | LIKELY | PCT CHANGE     | Gov't Acctg |
| INVESTMENT (MM \$)         |               |           |        |                |             |
| BATTERY LIMIT              |               |           | 2.78   |                | 2.78        |
| OFFSITE AND ALLOCATED AUX. |               |           | .90    |                | .90         |
| TOTAL (MM \$)              |               |           | 3.68   | 10             | 3.68        |

PROCESSING COST (CENTS/LB)

|                  |              |                   |        |     |      |
|------------------|--------------|-------------------|--------|-----|------|
| DEPRECIATION     |              | 10.0 PCT INVT     | 1.24   |     | -    |
| RM AND RL        |              | 5.0 PCT INVT      | .92(1) |     | .46  |
| OPERATING LABOR  | 12.00 MEN    | 8600.0 \$/MAN-YR  | .52    | 126 | .52  |
| CHEMICAL CONTROL | 4.00 MEN     | 10000.0 \$/MAN-YR | .20    | 325 | .20  |
| SUPERVISION      | 4.00 MEN     | 12000.0 \$/MAN-YR | .24    | 270 | .24  |
| ELECTRICITY      | .20 KWH/LB   | 1.0 CNT/KWH       | .20    | 406 | .20  |
| STEAM            | 4.00 LB /LB  | 75.0 CNT/LB       | .30    | 270 | .30  |
| WATER            | 10.00 GAL/LB | 10.0 CNT/GAL      | .10    | 811 | .10  |
| FUEL             | .01 GAL/LB   | 7.0 CNT/GAL       | .10    | 773 | .10  |
| TOTAL (CENTS/LB) |              |                   | 4.42   |     | 2.12 |

RAW MATERIAL COST (CENTS/LB)

|                  |               |               |      |     |      |
|------------------|---------------|---------------|------|-----|------|
| UREA             | 1.23200 LB/LB | 4.00 CNT/LB   | 4.93 | 16  | 4.93 |
| AMMONIUM NITRATE | .65600 LB/LB  | 2.50 CNT/LB   | 1.64 | 48  | 1.64 |
| CATALYST         | .00100 LB/LB  | 150.00 CNT/LB | .15  | 530 | .15  |
| TOTAL (CENTS/LB) |               |               | 6.72 |     | 6.72 |

PLANT OVERHEAD (CENTS/LB)

|  |  |  |       |  |      |
|--|--|--|-------|--|------|
| TOTAL MILL COST (CENTS/LB) EX BY-PRODUCT CREDITS |  |  | 11.58 |  | .45  |
|  |  |  |       |  | 9.29 |

BY-PRODUCT CREDIT (CENTS/LB)

|                    |              |            |     |  |     |
|--------------------|--------------|------------|-----|--|-----|
| AMMONIUM CARBAMATE | .60100 LB/LB | .00 CNT/LB | .00 |  | .00 |
| TOTAL (CENTS/LB)   |              |            | .00 |  | .00 |

|   |  |  |       |  |      |
|---|--|--|-------|--|------|
| TOTAL MILL COST (CENTS/LB) INC BY-PRODUCT CREDITS |  |  | 11.58 |  | 9.29 |
|---|--|--|-------|--|------|

fringe 2.02

\* 10 YEAR PLANT LIFE, EXISTING SITE  
15 PCT INDIRECT

Price 0% Return 11.31¢/lb

\*\* PERCENT CHANGE NEEDED TO AFFECT RETURN BY 2 PERCENTAGE POINTS

(1) 50% is maintenance material

RETURN CALCULATION

|              |    |     |    |
|--------------|----|-----|----|
| PLANT INVEST | \$ | 3.7 | MM |
| COOP ALLOC   | \$ | .1  | MM |
| WORKING CAP  | \$ | .4  | MM |
| TOTAL ASSETS | \$ | 4.1 | MM |

|                         |               |
|-------------------------|---------------|
| PRICE FOR 0 PCT RETURN  | 19.6 CENTS/LB |
| PRICE FOR 20 PCT RETURN | 19.6 CENTS/LB |
| PRICE FOR 30 PCT RETURN | 20.0 CENTS/LB |

FEASIBILITY STUDY - GUANIDINE NITRATE  
 WAF NO. 210

Basis: Cont. Process; 2 hr. reaction  
 AN/U/Cat. = 2/2/1.7  
 U Yld. = 87%; U Conv. = 88%  
 Yld. on AN = 100%

# ESTIMATED COSTS

PLANT CAPACITY 40.0 X 10<sup>3</sup> LB/YR

PROCESSIBILITY

|                            | UNIT | WATER/UNIT | 100% U/CAT. RATIO | Gov't Acctg |
|----------------------------|------|------------|-------------------|-------------|
| INVESTMENT (MM \$)         |      |            |                   |             |
| BATTERY LIMIT              |      |            | 4.87              | 4.84        |
| OFFSITE AND ALLOCATED AUX. |      |            | 1.00              | 1.00        |
| TOTAL (MM \$)              |      |            | 5.87              | 5.84        |

## PROCESSING COST (CENTS/LB)

|                  |              |                  |        |      |
|------------------|--------------|------------------|--------|------|
| DEPRECIATION     |              | 10.0 PCT INVEST  | 1.46   | -    |
| MAN AND RL       |              | 5.0 PCT INVEST   | .73(1) | .37  |
| OPERATING LABOR  | 12.00 XEN    | 8600.0 \$/YR-YR  | .26    | .26  |
| CHEMICAL CONTROL | 4.00 XEN     | 10000.0 \$/YR-YR | .10    | .10  |
| SUPERVISION      | 4.00 XEN     | 10000.0 \$/YR-YR | .10    | .12  |
| ELECTRICITY      | .20 KWH/LB   | 1.0 CNTZ-KWH     | .20    | .20  |
| STEAM            | 4.00 LB/LB   | 75.0 CNTZ-LB     | .30    | .30  |
| WATER            | 10.00 GAL/LB | 10.0 CNTZ-GAL    | .10    | .10  |
| FUEL             | .01 GAL/LB   | 7.0 CNTZ-GAL     | .10    | .10  |
| TOTAL (CENTS/LB) |              |                  | 5.27   | 1.55 |

## RAW MATERIAL COST (CENTS/LB)

|                  |               |                |      |      |
|------------------|---------------|----------------|------|------|
| UREA             | 1.13000 LB/LB | 4.00 CNTZ-LB   | 1.53 | 4.53 |
| AMMONIUM NITRATE | .65600 LB/LB  | 2.50 CNTZ-LB   | 1.64 | 1.64 |
| CATALYST         | .00200 LB/LB  | 150.00 CNTZ-LB | .30  | .30  |
| TOTAL (CENTS/LB) |               |                | 3.47 | 6.47 |

## PLANT OVERHEAD (CENTS/LB)

|  |  |  |       |      |
|--|--|--|-------|------|
| TOTAL MILL COST (CENTS/LB) EX BY-PRODUCT CREDITS |  |  | 10.12 | 8.30 |
|--|--|--|-------|------|

## BY-PRODUCT CREDIT (CENTS/LB)

|                    |              |             |     |     |
|--------------------|--------------|-------------|-----|-----|
| AMMONIUM CARBAMATE | .60000 LB/LB | .01 CNTZ-LB | .01 | .00 |
| TOTAL (CENTS/LB)   |              |             | .01 | .00 |

|   |  |  |       |      |
|---|--|--|-------|------|
| TOTAL MILL COST (CENTS/LB) INC BY-PRODUCT CREDITS |  |  | 10.12 | 8.30 |
|---|--|--|-------|------|

Fringe

Price 0% return 1.78 10.08¢/lb

\* 10 YEAR PLANT LIFE, EXISTING SILE  
 15 PCT INDIRECT

\* PERCENT CHARGE BEARING TO EFFECT SETTING OF OVERHEAD COST

(1) 50% is maintenance material

## OTHER CALCULATIONS

|              |      |
|--------------|------|
| PLANT INVEST | 4.87 |
| COPIE RELUC  | 1.00 |
| WORKING CAP  | 1.00 |
| TOTAL INVEST | 6.87 |

|                          |               |
|--------------------------|---------------|
| PRICE FOR 100 PCT U/CAT. | 11.00 CNTZ/LB |
| PRICE FOR 20 PCT U/CAT.  | 15.80 CNTZ/LB |
| PRICE FOR 30 PCT U/CAT.  | 16.00 CNTZ/LB |

COST STUDY - GUANIDINE NITRATE  
CASE NO. 220

Basis: Cont. Process; 3 hr. reaction  
AN/U/Cat. = 2/2/1.7  
U Yld. = 88%; U Conv. = 98%  
Yld. on AN = 100%

\*PRODUCTION COSTS

| PLANT CAPACITY                                    | 40.0 MM LB/YR | UNITS | RATE/UNIT         | LIKELY          | **SENSITIVITY |        | Gov't<br>Acctg |
|---|---------------|-------|-------------------|-----------------|---------------|--------|----------------|
|   |               |       |                   |                 | PCI           | CHANGE |                |
| INVESTMENT (MM \$)                                |               |       |                   |                 |               |        |                |
| BATTERY LIMIT                                     |               |       |                   | 5.61            |               |        | 5.61           |
| OFFSITE AND ALLOCATED AUX.                        |               |       |                   | 1.00            |               |        | 1.00           |
| TOTAL (MM \$)                                     |               |       |                   | 6.61            | 10            |        | 6.61           |
| PROCESSING COST (CENTS/LB)                        |               |       |                   |                 |               |        |                |
| DEPRECIATION                                      |               |       | 10.0 PCT INVEST   | 1.65            |               |        | -              |
| MM AND RL   |               |       | 5.0 PCT INVEST    | .83             |               |        | .42            |
| OPERATING LABOR                                   | 12.00 MEN     |       | 8600.0 \$/MAN-YR  | .26             | 227           |        | .26            |
| CHEMICAL CONTROL                                  | 4.00 MEN      |       | 10000.0 \$/MAN-YR | .10             | 585           |        | .10            |
| SUPERVISION                                       | 4.00 MEN      |       | 12000.0 \$/MAN-YR | .12             | 487           |        | .12            |
| ELECTRICITY                                       | .20 KWH/LB    |       | 1.0 CENTS/KWH     | .20             | 365           |        | .20            |
| STEAM   | 4.00 LB /LB   |       | 75.0 CENTS/LB     | .30             | 240           |        | .30            |
| WATER   | 10.00 GAL/LB  |       | 10.0 CENTS/GAL    | .10             | 731           |        | .10            |
| FUEL  | .01 GAL/LB    |       | 7.0 CENTS/GAL     | .10             | 696           |        | .10            |
| TOTAL (CENTS/LB)                                  |               |       |                   | 3.66            |               |        | 6.56           |
| RAW MATERIAL COST (CENTS/LB)                      |               |       |                   |                 |               |        |                |
| UREA  | 1.11800 LB/LB |       | 4.00 CENTS/LB     | 4.47            | 16            |        | 4.47           |
| AMMONIUM NITRATE                                  | .65600 LB/LB  |       | 2.50 CENTS/LB     | 1.64            | 44            |        | 1.64           |
| CATALYST  | .00300 LB/LB  |       | 159.00 CENTS/LB   | .45             | 159           |        | .45            |
| TOTAL (CENTS/LB)                                  |               |       |                   | 6.56            |               |        | 6.56           |
| PLANT OVERHEAD (CENTS/LB)                         |               |       |                   | .31             |               |        | .31            |
| TOTAL MILL COST (CENTS/LB) EX BY-PRODUCT CREDITS  |               |       |                   | 10.53           |               |        | 8.47           |
| BY-PRODUCT CREDIT (CENTS/LB)                      |               |       |                   |                 |               |        |                |
| AMMONIUM CARBAMATE                                | .60000 LB/LB  |       | .00 CENTS/LB      | .00             |               |        | .00            |
| TOTAL (CENTS/LB)                                  |               |       |                   | .00             |               |        | .00            |
| TOTAL MILL COST (CENTS/LB) INC BY-PRODUCT CREDITS |               |       |                   | 10.53           |               |        | 8.47           |
|   |               |       |                   | Fringe          |               |        | 1.87           |
|   |               |       |                   | Price 0% return |               |        | 10.34¢/lb      |

\* 10 YEAR PLANT LIFE, EXISTING SITE  
15 PCT INDIRECT

\*\* PERCENT CHANGE NEEDED TO AFFECT RETURN BY 2 PERCENTAGE POINTS

(1) 50% is maintenance material.

REFINED CALCULATIONS

|               |   |        |
|---------------|---|--------|
| PLANT INVEST  | 1 | 6.6 MM |
| CORP ALLOC    | 1 | .7 MM  |
| WORKING CAP   | 1 | .7 MM  |
| TOT OP ASSETS | 1 | 7.8 MM |

|                         |               |
|-------------------------|---------------|
| PRICE FOR 10 PCT RETURN | 10.0 CENTS/LB |
| PRICE FOR 20 PCT RETURN | 10.5 CENTS/LB |
| PRICE FOR 30 PCT RETURN | 11.0 CENTS/LB |



TEST STUDY - GUANIDINE NITRATE  
CASE NO. 301

Basis: Cont. Process; 1 hr. reaction  
AN/U/Cat. = 2/2/1.7  
U Yld. = 80%; U Conv. = 64.5%  
Aqueous Workup

\*PRODUCTION COSTS

| PLANT CAPACITY             | 40.0 MM LB/YR |           |             |             |      |
|----------------------------|---------------|-----------|-------------|-------------|------|
|                            | UNITS         | RATE/UNIT | ANNUAL COST | GOV'T ACCTG |      |
| INVESTMENT (MM \$)         |               |           |             |             |      |
| BATTERY LIMIT              |               |           | 3.69        |             | 3.69 |
| OFFSITE AND ALLOCATED AUX. |               |           | .90         |             | .90  |
| TOTAL (MM \$)              |               |           | 4.59        | 11          | 4.59 |

PROCESSING COST (CENTS/LB)

|                  |               |                   |     |      |
|------------------|---------------|-------------------|-----|------|
| DEPRECIATION     | 10.0 PCT 10YR | 1.15              |     | -    |
| MA AND RL        | 5.0 PCT 10YR  | .57 (1)           |     | .29  |
| OPERATING LABOR  | 10.00 MEN     | 8600.0 \$/MAN-YR  | .21 | .21  |
| CHEMICAL CONTROL | 4.00 MEN      | 10000.0 \$/MAN-YR | .13 | .10  |
| SUPERVISION      | 4.00 MEN      | 12000.0 \$/MAN-YR | .12 | .12  |
| ELECTRICITY      | .10 KWH/LB    | 1.00 CENTS/KWH    | .10 | .10  |
| STEAM            | 5.00 LB/LB    | 75.00 CENTS/LB    | .37 | .37  |
| WATER            | 8.00 GAL/LB   | 10.00 CENTS/GAL   | .08 | .08  |
| FUEL             | .01 GAL/LB    | 7.00 CENTS/GAL    | .10 | .10  |
| TOTAL (CENTS/LB) |               |                   |     | 1.37 |

RAW MATERIAL COST (CENTS/LB)

|                  |               |                 |      |  |
|------------------|---------------|-----------------|------|--|
| UREA             | 1.23200 LB/LB | 4.00 CENTS/LB   | 4.93 |  |
| AMMONIUM NITRATE | .65500 LB/LB  | 2.50 CENTS/LB   | 1.64 |  |
| CATALYST         | .00100 LB/LB  | 150.00 CENTS/LB | .15  |  |
| TOTAL (CENTS/LB) |               |                 | 6.72 |  |

PLANT OVERHEAD (CENTS/LB)

|   |  |  |      |  |
|---|--|--|------|--|
| TOTAL MILL COST (CENTS/LB) EX BY-PRODUCT CREDIT |  |  | 8.33 |  |
|---|--|--|------|--|

BY-PRODUCT CREDIT (CENTS/LB)

|  |              |              |      |      |
|--|--------------|--------------|------|------|
| AMMONIUM CARBONATE                               | .60000 LB/LB | .00 CENTS/LB | .00  |      |
| TOTAL (CENTS/LB)                                 |              |              | .00  |      |
| TOTAL MILL COST (CENTS/LB) INC BY-PRODUCT CREDIT |              |              | 8.33 |      |
|  |              |              |      | 1.73 |

Fringe

\* 10 YEAR PLANT LIFE, EXISTING SITE  
15 PCT INDIRECT

Price 0% return 10.06¢/lb

\*\* PERCENT CHANGE NEEDED TO AFFECT RETURN BY 2 PERCENT PER YEAR

(1) 50% is maintenance material

RETURN CALCULATION

|               |    |      |
|---------------|----|------|
| PLANT INVEST  | \$ | 4.59 |
| CORP ALLOC    | \$ | 1.15 |
| WORKING CAP   | \$ | 2.50 |
| TOT OP ASSETS | \$ | 8.24 |

|                         |                |
|-------------------------|----------------|
| PRICE FOR 10 PCT RETURN | 11.00 CENTS/LB |
| PRICE FOR 20 PCT RETURN | 12.00 CENTS/LB |
| PRICE FOR 30 PCT RETURN | 13.00 CENTS/LB |

COST STUDY - GUANIDINE NITRATE  
CASE NO.501

Basis: Cont. Process; 1 hr. reaction  
AN/U/Cat. = 2/2/1.7  
U Yld. = 80%; U Conv. = 64.5%  
Agitating reactor; melt workup

# \*PRODUCTION COSTS

| PLANT CAPACITY  | 40.0 MM LB/YR |                   |        | **SENSITIVITY   |             |
|---|---------------|-------------------|--------|-----------------|-------------|
|   | UNITS         | RATE/UNIT         | LIKELY | PCT CHANGE      | Gov't Acctg |
| INVESTMENT (MM \$)  |               |                   |        |                 |             |
| BATTERY LIMIT   |               |                   | 3.00   |                 | 3.00        |
| OFFSITE AND ALLOCATED AUX.                                    |               |                   | 1.00   |                 | 1.00        |
| TOTAL (MM \$)   |               |                   | 4.00   | 11              | 4.00        |
| PROCESSING COST (CENTS/LB)                                    |               |                   |        |                 |             |
| DEPRECIATION  |               | 10.0 PCT INVS     | 1.00   |                 | -           |
| MM AND RL   |               | 5.0 PCT INVS      | .50    | (1)             | .25         |
| OPERATING LABOR   | 12.00 MEN     | \$600.0 \$/MAN-YR | .26    | 143             | .26         |
| CHEMICAL CONTROL  | 4.00 MEN      | 10000.0 \$/MAN-YR | .10    | 370             | .10         |
| SUPERVISION   | 4.00 MEN      | 12000.0 \$/MAN-YR | .12    | 308             | .12         |
| ELECTRICITY   | .23 KWH/LB    | 1.0 CNT/KWH       | .23    | 201             | .23         |
| STEAM   | 4.00 LB /LB   | 75.0 CNT/LB       | .30    | 154             | .30         |
| WATER   | 10.00 GAL/LB  | 10.0 CNT/GAL      | .10    | 462             | .10         |
| FUEL  | .01 GAL/LB    | 7.0 CNT/GAL       | .10    | 440             | .10         |
| TOTAL (CENTS/LB)  |               |                   | 2.71   |                 | 1.46        |
| RAW MATERIAL COST (CENTS/LB)                                  |               |                   |        |                 |             |
| UREA  | 1.23200 LB/LB | 4.00 CNT/LB       | 4.93   | 9               | 4.93        |
| AMMONIUM NITRATE  | .65600 LB/LB  | 2.50 CNT/LB       | 1.64   | 28              | 1.64        |
| CATALYST  | .00100 LB/LB  | 150.00 CNT/LB     | .15    | 302             | .15         |
| TOTAL (CENTS/LB)  |               |                   | 6.72   |                 | 6.72        |
| PLANT OVERHEAD (CENTS/LB)                                     |               |                   | .23    |                 | .23         |
| TOTAL MILL COST (CENTS/LB) EX BY-PRODUCT CREDITS              |               |                   | 9.66   |                 | 8.41        |
| BY-PRODUCT CREDIT (CENTS/LB)                                  |               |                   |        |                 |             |
| AMMONIUM CARBAMATE  | .60000 LB/LB  | .00 CNT/LB        | .00    |                 | .00         |
| TOTAL (CENTS/LB)  |               |                   | .00    |                 | .00         |
| TOTAL MILL COST (CENTS/LB) INC BY-PRODUCT CREDITS             |               |                   | 9.66   |                 | 8.41        |
|   |               |                   |        | Fringe          | 1.74        |
|   |               |                   |        | Price 0% return | 10.15¢/lb   |
| 10 YEAR PLANT LIFE, EXISTING SITE                             |               |                   |        |                 |             |
| 15 PCT INDIRECT   |               |                   |        |                 |             |
| PERCENT CHANGE NEEDED TO AFFECT RETURN BY 1 PERCENTAGE POINTS |               |                   |        |                 |             |

(1) 50% is maintenance material

## RETURN CALCULATIONS

|               |    |        |
|---------------|----|--------|
| PLANT INVEST  | \$ | 4.0 MM |
| CORP ALLOC    | \$ | .1 MM  |
| WORKING CAP   | \$ | .6 MM  |
| TOT OP ASSETS | \$ | 4.7 MM |

|                         |               |
|-------------------------|---------------|
| PRICE FOR 0 PCT RETURN  | 11.4 CENTS/LB |
| PRICE FOR 20 PCT RETURN | 14.1 CENTS/LB |
| PRICE FOR 30 PCT RETURN | 15.8 CENTS/LB |

DOCS STUDY - GUANIDINE NITRATE Basis: Cont. Process; 1 hr. reaction  
 CASE NO. 610 AN/U = 0.75; aqueous workup  
 U Yld. = 71%; U Conv. = 66.5%

# REPRODUCTION COSTS

| PLANT CAPACITY             | 40.0 MM LB/YR |           |        | SENSITIVITY<br>PCT | Gov't<br>Acctg |
|----------------------------|---------------|-----------|--------|--------------------|----------------|
|                            | UNITS         | POTENTIAL | LIKELY | CHANGE             |                |
| INVESTMENT (MM \$)         |               |           |        |                    |                |
| BATTERY LIMIT              |               |           | 3.57   |                    | 3.57           |
| OFFSITE AND ALLOCATED AUX. |               |           | .90    |                    | .90            |
| TOTAL (MM \$)              |               |           | 4.47   | 11                 | 4.47           |

## PROCESSING COST (CENTS/LB)

|                  |             |                    |      |      |      |
|------------------|-------------|--------------------|------|------|------|
| DEPRECIATION     |             | 10.0 PCT IN 10 YR  | 1.12 |      | -    |
| MAN AND RL       |             | 5.0 PCT INVEST     | .56  | (1)  | .28  |
| OPERATING LABOR  | 10.00 HRN   | 8600.0 \$/YR - YR  | .21  | 1.21 | .21  |
| CHEMICAL CONTROL | 4.00 HRN    | 10000.0 \$/YR - YR | .10  | .11  | .10  |
| SUPERVISION      | 4.00 HRN    | 12000.0 \$/YR - YR | .10  | .12  | .12  |
| ELECTRICITY      | .10 KWH/LB  | 1.0 CENTS - YR     | .10  | .10  | .10  |
| STEAM            | 5.00 LB /LB | 75.0 CENTS - YR    | .47  | .47  | .37  |
| WATER            | 8.00 GAL/LB | 10.0 CENTS - YR    | .08  | .08  | .08  |
| FUEL             | .01 GAL/LB  | 7.0 CENTS - YR     | .07  | .07  | .10  |
| TOTAL (CENTS/LB) |             |                    | 1.77 |      | 1.36 |

## RAW MATERIAL COST (CENTS/LB)

|                  |               |              |      |  |      |
|------------------|---------------|--------------|------|--|------|
| GUAN.            | 1.38600 LB/LB | 4.00 CENTS   | 5.54 |  | 5.54 |
| AMMONIUM NITRATE | .65600 LB/LB  | 2.50 CENTS   | 1.64 |  | 1.64 |
| CATALYST         | .00100 LB/LB  | 150.00 CENTS | .15  |  | .15  |
| TOTAL (CENTS/LB) |               |              | 7.33 |  | 7.33 |

## PLANT OVERHEAD (CENTS/LB)

|   |       |  |     |  |      |
|---|-------|--|-----|--|------|
| TOTAL MILL COST (CENTS/LB) BY BY-PRODUCT CREDIT | 10.80 |  | .23 |  | 8.92 |
|---|-------|--|-----|--|------|

## BY-PRODUCT CREDIT (CENTS/LB)

|                    |              |           |     |  |     |
|--------------------|--------------|-----------|-----|--|-----|
| AMMONIUM CARBONATE | .60000 LB/LB | .00 CENTS | .00 |  | .00 |
| TOTAL (CENTS/LB)   |              |           | .00 |  | .00 |

|   |       |  |      |  |  |
|---|-------|--|------|--|--|
| TOTAL MILL COST (CENTS/LB) LESS BY-PRODUCT CREDIT | 10.80 |  | 8.92 |  |  |
|---|-------|--|------|--|--|

Fringe 1.86

Price 0% return 10.78¢/lb

10 YEAR PLANT LIFE, EXISTING SITE  
 15 PCT INDIRECT

PERCENT CHANGE NEEDED TO AFFECT RETURN BY 10.78¢/lb

(1) 50% is maintenance material

COST STUDY - GUANIDINE NITRATE Basis: Cont. Process; 1 hr. reaction  
CASE NO. 620 An/U = 0.56; aqueous workup  
U Yld. = 62.5%; U Conv. = 68%

\*PRODUCTION COSTS

| PLANT CAPACITY             | 40.0 MM LB/YR |           |        | **SENSITIVITY |             |
|----------------------------|---------------|-----------|--------|---------------|-------------|
|                            | UNITS         | RATE/UNIT | LIKELY | PCT CHANGE    | Gov't Acctg |
| INVESTMENT (MM \$)         |               |           |        |               |             |
| BATTERY LIMIT              |               |           | 3.60   |               | 3.60        |
| OFFSITE AND ALLOCATED AUX. |               |           | .90    |               | .90         |
| TOTAL (MM \$)              |               |           | 4.50   | 11            | 4.50        |

PROCESSING COST (CENTS/LB)

|                  |             |                   |         |     |      |
|------------------|-------------|-------------------|---------|-----|------|
| DEPRECIATION     |             | 10.0 PCT INVEST   | 1.12    |     | -    |
| RM AND RL        |             | 5.0 PCT INVEST    | .56 (1) |     | .28  |
| OPERATING LABOR  | 10.00 MEN   | 8600.0 \$/MAN-YR  | .21     | 194 | .21  |
| CHEMICAL CONTROL | 4.00 MEN    | 10000.0 \$/MAN-YR | .10     | 418 | .10  |
| SUPERVISION      | 4.00 MEN    | 12000.0 \$/MAN-YR | .12     | 348 | .12  |
| ELECTRICITY      | .10 KWH/LB  | 1.0 CENTS/KWH     | .10     | 500 | .10  |
| STEAM            | 5.00 LB/LB  | 75.0 CENTS/LB     | .37     | 1.9 | .37  |
| WATER            | 8.00 GAL/LB | 10.0 CENTS/GAL    | .08     | 683 | .08  |
| FUEL             | .01 GAL/LB  | 7.0 CENTS/GAL     | .10     | 498 | .10  |
| TOTAL (CENTS/LB) |             |                   | 2.78    |     | 1.36 |

RAW MATERIAL COST (CENTS/LB)

|                  |               |                 |      |     |      |
|------------------|---------------|-----------------|------|-----|------|
| UREA             | 1.57600 LB/LB | 4.00 CENTS/LB   | 6.30 | 8   | 6.30 |
| AMMONIUM NITRATE | .65600 LB/LB  | 2.50 CENTS/LB   | 1.64 | 31  | 1.64 |
| CATALYST         | .00100 LB/LB  | 150.00 CENTS/LB | .15  | 301 | .15  |
| TOTAL (CENTS/LB) |               |                 | 8.09 |     | 8.09 |

PLANT OVERHEAD (CENTS/LB)

|  |  |  |       |  |      |
|--|--|--|-------|--|------|
| TOTAL MILL COST (CENTS/LB) EX BY-PRODUCT CREDITS |  |  | .24   |  | .24  |
|  |  |  | 11.11 |  | 9.69 |

BY-PRODUCT CREDIT (CENTS/LB)

|   |              |              |       |  |      |
|---|--------------|--------------|-------|--|------|
| AMMONIUM CARBAMATE                                | .60000 LB/LB | .00 CENTS/LB | .00   |  | .00  |
| TOTAL (CENTS/LB)                                  |              |              | .00   |  | .00  |
| TOTAL MILL COST (CENTS/LB) INC BY-PRODUCT CREDITS |              |              | 11.11 |  | 9.69 |

Fringe 1.99

- \* 10 YEAR PLANT LIFE, EXISTING SITE Price 0% return 11.68¢/lb  
15 PCT INDIRECT  
\*\* PERCENT CHANGE NEEDED TO AFFECT RETURN BY 1.00 PRICE POINTS

(1) 50% is maintenance material

RETURN CALCULATION

|               |      |
|---------------|------|
| PLANT INVEST  | 4.50 |
| COMP ALLOC    | 1.12 |
| WORKING CAP   | 1.12 |
| TOT OP ASSETS | 6.74 |

|                       |                |
|-----------------------|----------------|
| PRICE FOR 10 PCT RETN | 11.11 CENTS/LB |
| PRICE FOR 20 PCT RETN | 12.11 CENTS/LB |
| PRICE FOR 30 PCT RETN | 13.11 CENTS/LB |

LAST STUDY - GUANIDINE NITRATE  
CASE NO.630

Basis: Cont. Process; 1 hr. reaction  
AN/U = 0.5; aqueous workup  
U Yld. = 59%; U Conv. = 68.5%

# PRODUCTION COSTS

| PLANT CAPACITY   | 40.0 MM LB/YR |                   |        |                 | SENSITIVITY<br>PCT | Gov't<br>Acctg |
|--|---------------|-------------------|--------|-----------------|--------------------|----------------|
|  | UNITS         | DATE/UNIT         | LINELY | CHANGE          |                    |                |
| INVESTMENT (MM \$)   |               |                   |        |                 |                    |                |
| BATTERY LIMIT  |               |                   | 5.57   |                 |                    | 3.57           |
| OFFSITE AND ALLOCATED AUX.   |               |                   | .90    |                 |                    | .90            |
| TOTAL (MM \$)  |               |                   | 6.47   | 11              |                    | 4.47           |
| PROCESSING COST (CENTS/LB)   |               |                   |        |                 |                    |                |
| DEPRECIATION   |               | 10.0 PCT INVEST   | 1.12   |                 |                    | .-             |
| WM AND RL  |               | 5.0 PCT INVEST    | .56    | (1)             |                    | .28            |
| OPERATING LABOR  | 10.00 MEN     | 8600.0 \$/MAN-YR  | .21    | 100             |                    | .21            |
| CHEMICAL CONTROL   | 4.00 MEN      | 10000.0 \$/MAN-YR | .19    | 417             |                    | .10            |
| SUPERVISION  | 4.00 MEN      | 12000.0 \$/MAN-YR | .12    | 266             |                    | .12            |
| ELECTRICITY  | .10 KWH/LB    | 1.0 CENTS/KWH     | .10    | 500             |                    | .10            |
| STEAM  | 5.00 LB/LB    | 75.0 CENTS/LB     | .37    | 130             |                    | .37            |
| WATER  | 8.00 GAL/LB   | 10.0 CENTS/GAL    | .08    | 680             |                    | .08            |
| FOIL   | .01 LB/LB     | 7.0 CENTS/LB      | .10    | 500             |                    | .10            |
| TOTAL (CENTS/LB)   |               |                   | 5.77   |                 |                    | 1.36           |
| RAW MATERIAL COST (CENTS/LB)   |               |                   |        |                 |                    |                |
| UREA   | 1.66800 LB/LB | 4.00 CENTS/LB     | 6.67   | 8               |                    | 6.67           |
| AMMONIUM NITRATE   | .65600 LB/LB  | 2.50 CENTS/LB     | 1.64   | 31              |                    | 1.64           |
| CATALYST   | .00100 LB/LB  | 150.00 CENTS/LB   | .15    | 201             |                    | .15            |
| TOTAL (CENTS/LB)   |               |                   | 8.46   |                 |                    | 8.46           |
| PLANT OVERHEAD (CENTS/LB)  |               |                   | .23    |                 |                    | .23            |
| TOTAL WILL COST (CENTS/LB) EX. BY-PRODUCT CREDIT                     |               |                   | 11.57  |                 |                    | 10.05          |
| BY-PRODUCT CREDIT (CENTS/LB)   |               |                   |        |                 |                    |                |
| AMMONIUM CARBAMATE   | .60000 LB/LB  | .00 CENTS/LB      | .00    |                 |                    | .00            |
| TOTAL (CENTS/LB)   |               |                   | .00    |                 |                    | .00            |
| TOTAL WILL COST (CENTS/LB) INC BY-PRODUCT CREDIT                     |               |                   | 11.57  |                 |                    | 10.05          |
|  |               |                   |        | Fringe          |                    | 2.03           |
|  |               |                   |        | Price 0% return |                    | 12.08¢/lb      |
| 10 YEAR PLANT LIFE, EXISTING SITE                                    |               |                   |        |                 |                    |                |
| 15 PCT INDIRECT  |               |                   |        |                 |                    |                |
| 50 PERCENT CHANGE NEEDED TO AFFECT RETURN BY 0.00% INCREASE IN COSTS |               |                   |        |                 |                    |                |

(1) 50% is maintenance material

RETURN CALCULATED

PLANT INVEST . . . . .  
COMP ALLOC . . . . .  
WORKING CAP . . . . .  
TOTAL INVESTMENT . . . . .

PRICE FOR 10 PCT RETN . . . . .  
PRICE FOR 20 PCT RETN . . . . .  
PRICE FOR 30 PCT RETN . . . . .

COST STUDY - GUANIDINE NITRATE  
CASE NO. 640

Basis: Cont. Process; 1 hr. reaction  
AN/U = 2; aqueous workup  
U Yld. = 99%; U Conv. = 55.5%

\*PRODUCTION COST

| PLANT CAPACITY   |  | 40.0 EA LB/YR |                   | **SENSITIVITY |                 | Govt     |
|--|--|---------------|-------------------|---------------|-----------------|----------|
|  |  | UNITS         | RATE/UNIT         | LINELY        | PCT CHANGE      | Accty    |
| INVESTMENT (MM \$)   |  |               |                   |               |                 |          |
| BATTERY LIMIT  |  |               |                   | 5.16          |                 | 5.16     |
| OFFSITE AND ALLOCATED AMX.                                       |  |               |                   | 1.00          |                 | 1.00     |
| TOTAL (MM \$)  |  |               |                   | 6.16          | 11              | 6.16     |
| PROCESSING COST (CENTS/LB)                                       |  |               |                   |               |                 |          |
| DEPRECIATION   |  |               | 10.0 PCT 1 YR     | 1.56          | (1)             | -        |
| AM AND RL  |  |               | 5.0 PCT 1 YR      | .77           |                 | .39      |
| OPERATING LABOR  |  | 10.00 MEN     | 8000.0 \$/MAN-YR  | .21           | 253             | .21      |
| CHEMICAL CONTROL   |  | 4.00 MEN      | 10000.0 \$/MAN-YR | .10           | 564             | .10      |
| SUPERVISION  |  | 4.00 MEN      | 12000.0 \$/MAN-YR | .12           | 454             | .12      |
| ELECTRICITY  |  | .20 KWH/LB    | 1.0 CENTS/KWH     | .20           | 340             | .20      |
| STEAM  |  | 6.00 LB/LB    | 75.0 CENTS/LB     | .25           | 151             | .45      |
| WATER  |  | 10.00 GAL/LB  | 10.0 CENTS/GAL    | .10           | 681             | .10      |
| FUEL   |  | .02 GAL/LB    | 7.0 CENTS/GAL     | .14           | 486             | .14      |
| TOTAL (CENTS/LB)   |  |               |                   | 3.63          |                 | 1.71     |
| RAW MATERIAL COST (CENTS/LB)                                     |  |               |                   |               |                 |          |
| UREA   |  | .99500 LB/LB  | 4.10 CENTS/LB     | 4.08          | 17              | 3.98     |
| AMMONIUM NITRATE   |  | .65600 LB/LB  | 2.80 CENTS/LB     | 1.84          | 41              | 1.64     |
| CATALYST   |  | .00200 LB/LB  | 150.00 CENTS/LB   | .30           | 999             | .30      |
| TOTAL (CENTS/LB)   |  |               |                   | 5.99          |                 | 5.92     |
| PLANT OVERHEAD (CENTS/LB)  |  |               |                   | .08           |                 | .28      |
| TOTAL MILL COST (CENTS/LB) EX BY-PRODUCT CREDIT                  |  |               |                   | 6.84          |                 | 7.91     |
| BY-PRODUCT CREDIT (CENTS/LB)                                     |  |               |                   |               |                 |          |
| AMMONIUM CARBONATE   |  | .60000 LB/LB  | .00 CENTS/LB      | .00           |                 | .00      |
| TOTAL (CENTS/LB)   |  |               |                   | .00           |                 | .00      |
| TOTAL MILL COST (CENTS/LB) INC BY-PRODUCT CREDIT                 |  |               |                   | 6.84          |                 | 7.91     |
|  |  |               |                   |               | Fringe          | 1.76     |
|  |  |               |                   |               | Price 0% return | 9.67¢/lb |
| * 10 YEAR PLANT LIFE, EXISTING SITE                              |  |               |                   |               |                 |          |
| 15 PCT INDIRECT  |  |               |                   |               |                 |          |
| ** PERCENT CHANGE NEEDED TO AFFECT RETURN BY 1 PERCENTAGE POINTS |  |               |                   |               |                 |          |

(1) 50% is maintenance material

RETURN CALCULATION

|                  |         |
|------------------|---------|
| PLANT INVESTMENT | 6.16 MM |
| CORR. OVERTIME   | .00 MM  |
| OPERATING COST   | .00 MM  |
| TOTAL INVESTMENT | 6.16 MM |

|                         |               |
|-------------------------|---------------|
| PRICE FOR 10 PCT RETURN | 11.0 CENTS/LB |
| PRICE FOR 20 PCT RETURN | 18.7 CENTS/LB |
| PRICE FOR 30 PCT RETURN | 17.7 CENTS/LB |

COST STUDY - GUANIDINE NITRATE  
CASE NO. 650

Basis: Cont. Process; 1 hr. reaction  
AN/U = 1.5; aqueous workup  
U Yld. = 92.5%; U Conv. = 60%

# PRODUCTION COSTS

| PLANT CAPACITY             | 400.0 MM LB/YR |       |           |                     | GOVERNMENTALITY |
|----------------------------|----------------|-------|-----------|---------------------|-----------------|
|                            |                | UNITS | RATE/UNIT | LIBERALLY ESTIMATED | Govt Acctg      |
| INVESTMENT (MM \$)         |                |       |           |                     |                 |
| BATTERY LIMIT              |                |       |           |                     | 4.26            |
| OFFSITE AND ALLOCATED AUX. |                |       |           |                     | .95             |
| TOTAL (MM \$)              |                |       |           |                     | 5.21            |

## PROCESSING COST (CENTS/LB)

|                  |             |                   |      |     |      |
|------------------|-------------|-------------------|------|-----|------|
| DEPRECIATION     |             | 10.0 PCT INVEST   | 1.50 |     |      |
| MA AND RL        |             | 5.0 PCT INVEST    | .75  | (1) | .33  |
| OPERATING LABOR  | 10.00 MEN   | 8600.0 \$/MAN-YR  | .91  | 217 | .21  |
| CHEMICAL CONTROL | 4.00 MEN    | 10000.0 \$/MAN-YR | .10  | 218 | .10  |
| SUPERVISION      | 4.00 MEN    | 12000.0 \$/MAN-YR | .12  | 229 | .12  |
| ELECTRICITY      | .15 KWH/LB  | 1.0 CNT/KWH       | .15  | 349 | .15  |
| STEAM            | 5.00 LB/LB  | 75.0 CNT/LB       | .37  | 155 | .37  |
| WATER            | 9.00 GAL/LB | 10.0 CNT/GAL      | .09  | 304 | .09  |
| FUEL             | .02 GAL/LB  | 7.0 CNT/GAL       | .14  | 300 | .12  |
| TOTAL (CENTS/LB) |             |                   | 5.12 |     | 1.49 |

## RAW MATERIAL COST (CENTS/LB)

|                  |               |             |      |     |      |
|------------------|---------------|-------------|------|-----|------|
| UREA             | 1.06400 LB/LB | 4.00 C/LB   | 4.26 | 12  | 4.26 |
| AMMONIUM NITRATE | .65600 LB/LB  | 2.50 C/LB   | 1.64 | 35  | 1.64 |
| CATALYST         | .00120 LB/LB  | 150.00 C/LB | .18  | 217 | .18  |
| TOTAL (CENTS/LB) |               |             | 6.08 |     | 6.08 |

## PLANT OVERHEAD (CENTS/LB)

|   |  |  |      |  |      |
|---|--|--|------|--|------|
| TOTAL MILL COST (CENTS/LB) EX BY-PRODUCT CREDIT |  |  | 6.95 |  | 7.83 |
|---|--|--|------|--|------|

## BY-PRODUCT CREDIT (CENTS/LB)

|                    |              |          |     |  |     |
|--------------------|--------------|----------|-----|--|-----|
| AMMONIUM CARBAMATE | .60000 LB/LB | .00 C/LB | .00 |  | .00 |
| TOTAL (CENTS/LB)   |              |          | .00 |  | .00 |

|  |  |  |  |  |      |
|--|--|--|--|--|------|
| TOTAL MILL COST (CENTS/LB) INC BY-PRODUCT CREDIT |  |  |  |  | 7.83 |
|--|--|--|--|--|------|

Fringe 1.65  
Price 0% return 9.48 ¢/lb

10 YEAR PLANT LIFE, EXISTING SITE  
15 PCT INDIRECT

PERCENT CHANGE NEEDED TO AFFECT RETURN BY PERCENTAGE 1.15%

(1) 50% is maintenance material

## REVENUE CALCULATIONS

|                  |                |
|------------------|----------------|
| PLANT THROUGHPUT | 400.0 MM LB/YR |
| COST ALLOWANCE   | 1.00 C/LB      |
| GOVERNMENTALITY  | 1.00 C/LB      |
| TOTAL REVENUE    | 400.0 MM \$/YR |

|                              |               |
|------------------------------|---------------|
| PRICE FOR 10 YEAR PLANT LIFE | 11.0 CENTS/LB |
| PRICE FOR 20 YEAR PLANT LIFE | 14.0 CENTS/LB |
| PRICE FOR 30 YEAR PLANT LIFE | 16.0 CENTS/LB |

COST STUDY - GUANIDINE NITRATE  
CASE NO.810

Basic Case  
Basis: Cont. Process  
AN/U/Cat. = 2/2/1.7  
U Yld. = 80% U Conv. = 64.5%  
AN Yld. = 100% AN Conv. = 32%  
\*PRODUCTION 1000 TONS By-Prod. Credit = 1¢/lb.

| PLANT CAPACITY             | 40.0 MM LB/YR | **SENSITIVITY |        |       |
|----------------------------|---------------|---------------|--------|-------|
|                            |               | PCT           | Gov't  |       |
|                            | UNITS         | NO. / UNIT    | CHANGE | Acctg |
| INVESTMENT (MM \$)         |               |               |        |       |
| BATTERY LIMIT              |               |               | 4.22   | 4.22  |
| OFFSITE AND ALLOCATED AUX. |               |               | 1.00   | 1.00  |
| TOTAL (MM \$)              |               |               | 5.22   | 5.22  |

| PROCESSING COST (CENTS/LB) |              |                   |         |     |      |
|----------------------------|--------------|-------------------|---------|-----|------|
| DEPRECIATION               |              | 10.00 PCT 15 YR   | 1.30    |     | -    |
| MM AND RL                  |              | 5.00 PCT 15 YR    | .65 (1) |     | .33  |
| OPERATING LABOR            | 12.00 MEN    | 8600.0 \$/MAN-YR  | .26     | 182 | .26  |
| CHEMICAL CONTROL           | 4.00 MEN     | 10000.0 \$/MAN-YR | .10     | 469 | .10  |
| SUPERVISION                | 4.00 MEN     | 12000.0 \$/MAN-YR | .12     | 391 | .12  |
| ELECTRICITY                | .20 KWH/LB   | 1.0 CENTS/KWH     | .20     | 203 | .20  |
| STEAM                      | 4.00 LB /LB  | 75.0 CENTS/LB     | .30     | 195 | .30  |
| WATER                      | 10.00 GAL/LB | 10.0 CENTS/GAL    | .10     | 586 | .10  |
| FUEL                       | .01 GAL/LB   | 7.0 CENTS/GAL     | .10     | 558 | .10  |
| TOTAL (CENTS/LB)           |              |                   | 3.12    |     | 1.51 |

| RAW MATERIAL COST (CENTS/LB) |               |                 |      |     |      |
|------------------------------|---------------|-----------------|------|-----|------|
| UREA                         | 1.23200 LB/LB | 4.00 CENTS/LB   | 4.93 | 12  | 4.93 |
| AMMONIUM NITRATE             | .65600 LB/LB  | 2.50 CENTS/LB   | 1.64 | 35  | 1.64 |
| CATALYST                     | .00100 LB/LB  | 150.00 CENTS/LB | .15  | 383 | .15  |
| TOTAL (CENTS/LB)             |               |                 | 6.72 |     | 6.72 |

| PLANT OVERHEAD (CENTS/LB)                       |  |  |       |  |      |
|---|--|--|-------|--|------|
|   |  |  | .27   |  | .27  |
| TOTAL MILL COST (CENTS/LB) EX BY-PRODUCT CREDIT |  |  | 10.12 |  | 8.50 |

| BY-PRODUCT CREDIT (CENTS/LB)                      |              |               |      |  |      |
|---|--------------|---------------|------|--|------|
| AMMONIUM CARBONATE                                | .60000 LB/LB | 1.00 CENTS/LB | .60  |  | .60  |
| TOTAL (CENTS/LB)                                  |              |               | .60  |  | .60  |
| TOTAL MILL COST (CENTS/LB) INC BY-PRODUCT CREDITS |              |               | 9.52 |  | 7.90 |

Fringe 1.68

Price 0% return 9.58¢/lb

- \* 10 YEAR PLANT LIFE, EXISTING SITE
- 15 PCT INDIRECT
- \* PERCENT CHANGE NEEDED TO AFFECT RETURN ON INVESTMENT

(1) 50% is maintenance material

RETURN CALCULATION

PLANT INVEST 4 8.0 MM  
CORP ALLOC 1 0.0 MM  
WORKING CAP 1 0.0 MM  
TOT OF ASSETS 4 8.0 MM

PRICE FOR 10 PCT RETURN 11.2 CENTS/LB  
PRICE FOR 20 PCT RETURN 12.7 CENTS/LB  
PRICE FOR 30 PCT RETURN 14.2 CENTS/LB



COST STUDY - GUANIDINE NITRATE Basis: Cont. Process  
CASE NO. 820

AN/U/Cat. = 2/2/1.7  
U Yld. = 80% U Conv. = 64.5%  
AN Yld. = 100% AN Conv. = 32%  
By-Prod. Credit = 2¢/lb.

\*PRODUCTION COSTS

| PLANT CAPACITY             | 40.0 MM LB/YR | *SENSITIVITY |        |        | Gov't |
|----------------------------|---------------|--------------|--------|--------|-------|
|                            | UNITS         | RATE/UNIT    | LINELY | CHANGY | Actg  |
| INVESTMENT (MM \$)         |               |              |        |        |       |
| BATTERY LIMIT              |               |              | 4.00   |        | 4.22  |
| OFFSITE AND ALLOCATED AUX. |               |              | 1.00   |        | 1.00  |
| TOTAL (MM \$)              |               |              | 5.00   | 1      | 5.22  |

| PROCESSING COST (CENTS/LB) |              |                  |        |      |      |
|----------------------------|--------------|------------------|--------|------|------|
| DEPRECIATION               |              | 10.0 PCT 15000   | 1.00   |      | -    |
| MAINT AND PL               |              | 5.0 PCT 15000    | .65(1) |      | .33  |
| OPERATING LABOR            | 12.00 MEN    | 8600.0 \$/HR-YR  | .26    | 121  | .26  |
| CHEMICAL CONTROL           | 4.00 MEN     | 10000.0 \$/HR-YR | .10    | 467  | .10  |
| SUPERVISION                | 4.00 MEN     | 12000.0 \$/HR-YR | .12    | 399  | .12  |
| ELECTRICITY                | .20 KWH/LB   | 1.0 CENTS/KWH    | .20    | 5.92 | .20  |
| STEAM                      | 4.00 LB /LB  | 75.0 CENTS/LB    | .30    | 1.25 | .30  |
| WATER                      | 10.00 GAL/LB | 10.0 CENTS/GAL   | .10    | 3.84 | .10  |
| FUEL                       | .01 GAL/LB   | 7.0 CENTS/GAL    | .10    | 3.56 | .10  |
| TOTAL (CENTS/LB)           |              |                  | 2.12   |      | 1.51 |

| RAW MATERIAL COST (CENTS/LB) |               |                 |      |     |      |
|------------------------------|---------------|-----------------|------|-----|------|
| AN                           | 1.23200 LB/LB | 4.00 CENTS/LB   | 4.93 | 12  | 4.93 |
| AMMONIUM NITRATE             | .65600 LB/LB  | 2.50 CENTS/LB   | 1.64 | 38  | 1.64 |
| CATALYST                     | .09100 LB/LB  | 150.00 CENTS/LB | .15  | 381 | .15  |
| TOTAL (CENTS/LB)             |               |                 | 6.72 |     | 6.72 |

|  |  |  |       |  |      |
|--|--|--|-------|--|------|
| PLANT OVERHEAD (CENTS/LB)                        |  |  | .27   |  | .27  |
| TOTAL MILL COST (CENTS/LB) INC BY-PRODUCT CREDIT |  |  | 11.12 |  | 8.50 |

| BY-PRODUCT CREDIT (CENTS/LB)                     |              |               |      |  |      |
|--|--------------|---------------|------|--|------|
| AMMONIUM CARBAMATE                               | .60000 LB/LB | 2.00 CENTS/LB | 1.20 |  | 1.20 |
| TOTAL (CENTS/LB)                                 |              |               | 1.20 |  | 1.20 |
| TOTAL MILL COST (CENTS/LB) INC BY-PRODUCT CREDIT |              |               | 9.92 |  | 7.30 |

Fringe 1.58

\* 10 YEAR PLANT LIFE, EXISTING SITE Price 0% return 8.88¢/lb

15 PCT INDIRECT

\* PERCENT CHANGE NEEDED TO AFFECT RETURN BY 1% DECREASE IN PRICE

(1) 50% is maintenance material

DETAILED COST BREAKDOWN

|             |      |
|-------------|------|
| PLANT 15000 | 1.00 |
| MAINT 15000 | .65  |
| LABOR 8600  | .26  |
| TOTAL 15000 | 1.91 |

|                        |                |
|------------------------|----------------|
| PRICE F = 10 PCT 15000 | 10.00 CENTS/LB |
| PRICE F = 20 PCT 15000 | 12.00 CENTS/LB |
| PRICE F = 30 PCT 15000 | 15.00 CENTS/LB |

COST STUDY - GUANIDINE NITRATE  
CASE NO. 830

Basis: Cont. Process

AN/U/Cat. = 2/2/1.7

U Yld. = 80%

U Conv. = 64.5%

AN Yld. = 100%

AN Conv. = 32%

By-Prod. Credit = 3¢/lb.

\*PRODUCTION COSTS

PLANT CAPACITY 40.0 MM LB/YR

\*\*SENSITIVITY

|                            | UNITS | RATE/UNIT | LIKELY | PCT CHANGE | Govt Acctg |
|----------------------------|-------|-----------|--------|------------|------------|
| INVESTMENT (MM \$)         |       |           |        |            |            |
| BATTERY LIMIT              |       |           | 4.22   |            | 4.22       |
| OFFSITE AND ALLOCATED AUX. |       |           | 1.00   |            | 1.00       |
| TOTAL (MM \$)              |       |           | 5.22   | 11         | 5.22       |

PROCESSING COST (CENTS/LB)

|                  |              |                    |         |     |      |
|------------------|--------------|--------------------|---------|-----|------|
| DEPRECIATION     |              | 10.0 PCT INVEST    | 1.30    |     | -    |
| MM AND RL        |              | 5.0 PCT INVEST     | .65 (1) |     | .33  |
| OPERATING LABOR  | 12.00 MEN    | 8600.0 \$/YEAR-YR  | .26     | 181 | .26  |
| CHEMICAL CONTROL | 4.00 MEN     | 10000.0 \$/YEAR-YR | .10     | 466 | .10  |
| SUPERVISION      | 4.00 MEN     | 12000.0 \$/YEAR-YR | .12     | 388 | .12  |
| ELECTRICITY      | .20 KWH/LB   | 1.0 CWT/5.0H       | .20     | 291 | .20  |
| STEAM            | 4.00 LB /LB  | 75.0 CWT/2.0H      | .30     | 194 | .30  |
| WATER            | 10.00 GAL/LB | 10.0 CWT/2.0H      | .10     | 582 | .10  |
| FUEL             | .01 GAL/LB   | 7.0 CWT/ GAL       | .10     | 554 | .10  |
| TOTAL (CENTS/LB) |              |                    | 3.14    |     | 1.51 |

RAW MATERIAL COST (CENTS/LB)

|                  |               |               |      |     |      |
|------------------|---------------|---------------|------|-----|------|
| UREA             | 1.23200 LB/LB | 4.00 CWT/LB   | 4.93 | 12  | 4.93 |
| AMMONIUM NITRATE | .65600 LB/LB  | 2.50 CWT/LB   | 1.64 | 35  | 1.64 |
| CATALYST         | .00100 LB/LB  | 150.00 CWT/LB | .15  | 380 | .15  |
| TOTAL (CENTS/LB) |               |               | 6.72 |     | 6.72 |

PLANT OVERHEAD (CENTS/LB)

|  |  |  |       |  |      |
|--|--|--|-------|--|------|
| TOTAL MILL COST (CENTS/LB) EX BY-PRODUCT CREDITS |  |  | 10.12 |  | .27  |
|  |  |  |       |  | 8.50 |

BY-PRODUCT CREDIT (CENTS/LB)

|   |              |             |      |  |      |
|---|--------------|-------------|------|--|------|
| AMMONIUM CARBAMATE                                | .60000 LB/LB | 3.00 CWT/LB | 1.80 |  | 1.80 |
| TOTAL (CENTS/LB)                                  |              |             | 1.80 |  | 1.80 |
| TOTAL MILL COST (CENTS/LB) INC BY-PRODUCT CREDITS |              |             | 8.72 |  | 6.70 |

Fringe

Price 0% return

1.48

\* 10 YEAR PLANT LIFE, EXISTING SITE

15 PCT INDIRECT

\*\* PERCENT CHANGE NEEDED TO AFFECT RETURN BY 2 PERCENTAGE POINTS

(1) 50% maintenance material

RETURN CALCULATIONS

|               |    |      |
|---------------|----|------|
| PLANT INVEST  | \$ | 5.22 |
| CORP ALLOC    | \$ | 1.00 |
| WORKING CAP   | \$ | 1.60 |
| TOT OP ASSETS | \$ | 7.82 |

|                         |               |
|-------------------------|---------------|
| PRICE FOR 0 PCT RETURN  | 11.5 CENTS/LB |
| PRICE FOR 20 PCT RETURN | 15.5 CENTS/LB |
| PRICE FOR 30 PCT RETURN | 18.5 CENTS/LB |

I-53

FEASIBILITY STUDY - GUANIDINE NITRATE  
CASE NO. 919

**Basis:** Basic Case  
Cont. Process  
AN/U/Cat. = 2/2/1.7  
U Yld. = 80% U Conv. = 64.5%  
AN Yld. = 100% AN Conv. = 32%  
Urea = 2¢/lb.

# PRODUCTION COSTS

| PLANT CAPACITY             | 40.0 MM LB/YR |      |            | PERCENTAGE | Govt  |
|----------------------------|---------------|------|------------|------------|-------|
|                            |               | UNIT | PRICE/UNIT | CHANGE     | Acctg |
| INVESTMENT (MM \$)         |               |      |            |            |       |
| BATTERY LIMIT              |               |      | 5.00       |            | 4.22  |
| OFFSITE AND ALLOCATED AUX. |               |      | 1.00       |            | 1.00  |
| TOTAL (MM \$)              |               |      | 5.00       | 10         | 5.22  |

| PROCESSING COST (CENTS/LB) |              |                    |      |     |      |
|----------------------------|--------------|--------------------|------|-----|------|
| DEPRECIATION               |              | 10.0 PCT 15 YR     | 1.30 |     | -    |
| MAN AND RL                 |              | 5.0 PCT 15 YR      | .65  | (1) | .33  |
| OPERATING LABOR            | 12.00 MEN    | 8600.0 1/2000 - Y  | .06  | 177 | .26  |
| CHEMICAL CONTROL           | 4.00 MEN     | 10000.0 1/2000 - Y | .10  | 200 | .10  |
| SUPERVISION                | 4.00 MEN     | 12000.0 1/2000 - Y | .10  | 240 | .12  |
| ELECTRICITY                | .20 KWH/LB   | 1.0 CENTS/KWH      | .20  | 200 | .20  |
| STEAM                      | 4.00 LB/LB   | 75.0 CENTS/LB      | .30  | 100 | .30  |
| WATER                      | 10.00 GAL/LB | 10.0 CENTS/GAL     | .10  | 500 | .10  |
| FOUL                       | .01 GAL/LB   | 7.0 CENTS/GAL      | .07  | 500 | .10  |
| TOTAL (CENTS/LB)           |              |                    | 5.15 |     | 1.51 |

| MATERIAL COST (CENTS/LB) |               |                 |      |     |      |
|--------------------------|---------------|-----------------|------|-----|------|
| UREA                     | 1.23200 LB/LB | 2.00 CENTS/LB   | .25  |     | 2.46 |
| AMMONIUM NITRATE         | .65600 LB/LB  | 2.50 CENTS/LB   | 1.64 |     | 1.64 |
| CATALYST                 | .00100 LB/LB  | 150.00 CENTS/LB | .15  | 375 | .15  |
| TOTAL (CENTS/LB)         |               |                 | 4.05 |     | 4.25 |

|  |  |  |      |  |      |
|--|--|--|------|--|------|
| PLANT OVERHEAD (CENTS/LB)                        |  |  | .27  |  | .27  |
| TOTAL MILL COST (CENTS/LB) EX BY-PRODUCT CREDITS |  |  | 7.66 |  | 6.03 |

| BY-PRODUCT CREDIT (CENTS/LB)                      |              |              |      |  |      |
|---|--------------|--------------|------|--|------|
| AMMONIUM CARBAMATE                                | .60000 LB/LB | .01 CENTS/LB | .01  |  | .00  |
| TOTAL (CENTS/LB)                                  |              |              | .01  |  | .00  |
| TOTAL MILL COST (CENTS/LB) INC BY-PRODUCT CREDITS |              |              | 7.66 |  | 6.03 |

Fringe 1.34

Price 0% return 7.37¢/lb

\* 10 YEAR PLANT LIFE, EXISTING SITE  
15 PCT INDIRECT

\*\* PERCENT CHANGE NEEDED TO AFFECT PRICES BY 10% INCREASE

(1) 50% is maintenance material

## REFINED CALCULATIONS

|                  |      |
|------------------|------|
| PLANT INVESTMENT | 5.22 |
| COST ALLOC.      | .33  |
| WORKING CAPITAL  | .33  |
| TOTAL OF 10 YR   | 5.88 |

|                       |             |
|-----------------------|-------------|
| PRICE FOR 10 YR PLANT | 1.00 PER YR |
| PRICE FOR 20 YR PLANT | 1.00 PER YR |
| PRICE FOR 30 YR PLANT | 1.00 PER YR |

QEST STUDY - GUANIDINE NITRATE  
CASE NO. 920

Basis: Cont. Process

AN/U/Cat. = 2/2/1.7

U Yld. = 80% U Conv. = 64.5%

AN Yld. = 100% AN Conv. = 32%

Urea = 3¢/lb.

\*PRODUCTION COSTS

PLANT CAPACITY 40.0 MM LB/YR

\*\*SENSITIVITY

|                            | UNITS | RATE/UNIT | LINEALLY | PCT CHANGE | Govt Acctg |
|----------------------------|-------|-----------|----------|------------|------------|
| INVESTMENT (MM \$)         |       |           |          |            |            |
| BATTERY LIMIT              |       |           | 4.00     |            | 4.22       |
| OFFSITE AND ALLOCATED AUX. |       |           | 1.00     |            | 1.00       |
| TOTAL (MM \$)              |       |           | 5.00     | 11         | 5.22       |

PROCESSING COST (CENTS/LB)

|                  |              |                   |         |     |      |
|------------------|--------------|-------------------|---------|-----|------|
| DEPRECIATION     |              | 10.0 PCT INVEST   | 1.30    |     | -    |
| MM AND RL        |              | 5.0 PCT INVEST    | .65 (1) |     | .33  |
| OPERATING LABOR  | 12.00 MEN    | 8600.0 \$/MAN-YR  | .26     | 180 | .26  |
| CHEMICAL CONTROL | 4.00 MEN     | 10000.0 \$/MAN-YR | .10     | 464 | .10  |
| SUPERVISION      | 4.00 MEN     | 12000.0 \$/MAN-YR | .12     | 387 | .12  |
| ELECTRICITY      | .20 KWH/LB   | 1.0 CWT/KWH       | .30     | 290 | .20  |
| STEAM            | 4.00 LB /LB  | 75.0 CWT/LB       | .30     | 193 | .30  |
| WATER            | 10.00 GAL/LB | 10.0 CWT/GAL      | .10     | 580 | .10  |
| FUEL             | .01 GAL/LB   | 7.0 CWT/GAL       | .10     | 552 | .10  |
| TOTAL (CENTS/LB) |              |                   | 3.14    |     | 1.51 |

RA MATERIAL COST (CENTS/LB)

|                  |               |               |      |     |      |
|------------------|---------------|---------------|------|-----|------|
| UREA             | 1.23200 LB/LB | 3.00 CWT/LB   | 3.70 | 15  | 3.70 |
| AMMONIUM NITRATE | .65600 LB/LB  | 2.50 CWT/LB   | 1.64 | 35  | 1.64 |
| CATALYST         | .00100 LB/LB  | 150.00 CWT/LB | .15  | 379 | .15  |
| TOTAL (CENTS/LB) |               |               | 5.49 |     | 5.49 |

PLANT OVERHEAD (CENTS/LB)

|  |  |  |      |  |      |
|--|--|--|------|--|------|
| TOTAL MILL COST (CENTS/LB) EX BY-PRODUCT CREDITS |  |  | 7.27 |  | 7.27 |
|--|--|--|------|--|------|

BY-PRODUCT CREDIT (CENTS/LB)

|   |              |            |      |  |      |
|---|--------------|------------|------|--|------|
| AMMONIUM CARBAMATE                                | .60000 LB/LB | .00 CWT/LB | .00  |  | .00  |
| TOTAL (CENTS/LB)                                  |              |            | .00  |  | .00  |
| TOTAL MILL COST (CENTS/LB) INC BY-PRODUCT CREDITS |              |            | 7.27 |  | 7.27 |

Fringe 1.61

\* 10 YEAR PLANT LIFE, EXISTING SITE

Price 0% return 8.88¢/lb

15 PCT INDIRECT

\*\* PERCENT CHANGE NEEDED TO AFFECT RETURN BY 1 PERCENTAGE POINTS

(1) 50% is maintenance material

RETURN CALCULATION

|              |    |      |
|--------------|----|------|
| PLANT INVEST | \$ | 5.22 |
| CORP ALLOC   | \$ | .00  |
| WORKING CAP  | \$ | .00  |
| TOTAL ASSETS | \$ | 5.22 |

|                         |               |
|-------------------------|---------------|
| PRICE FOR 10 PCT RETURN | 11.8 CENTS/LB |
| PRICE FOR 20 PCT RETURN | 12.7 CENTS/LB |
| PRICE FOR 30 PCT RETURN | 13.7 CENTS/LB |

COST STUDY - GUANIDINE NITRATE Basis: Cont. Process; 1 hr. reaction  
CASE NO. 710 AN/U/Cat. = 2/2/1.7  
Aqueous workup, 3-stage agit. reactor  
U Yld. = 80%; U Conv. = 64.5%

\*PRODUCTION COSTS

| PLANT CAPACITY  | 40.0 MM LB/YR |                   |        | **SENSITIVITY   |             |
|---|---------------|-------------------|--------|-----------------|-------------|
|   | UNITS         | RATE/UNIT         | LIKELY | PCT CHANGE      | Gov't Acctg |
| INVESTMENT (MM \$)  |               |                   |        |                 |             |
| BATTERY LIMIT   |               |                   | 2.49   |                 | 2.49        |
| OFFSITE AND ALLOCATED AUX.                                      |               |                   | .90    |                 | .90         |
| TOTAL (MM \$)   |               |                   | 3.39   | 11              | 3.30        |
| PROCESSING COST (CENTS/LB)                                      |               |                   |        |                 |             |
| DEPRECIATION  |               | 10.0 PCT INVEST   | .95    |                 | -           |
| MA AND RL   |               | 5.0 PCT INVEST    | .48    | (1)             | .21         |
| OPERATING LABOR   | 10.00 MEN     | 8600.0 \$/MAN-YR  | .91    | 148             | .21         |
| CHEMICAL CONTROL  | 4.00 MEN      | 10000.0 \$/MAN-YR | .10    | 319             | .10         |
| SUPERVISION   | 4.00 MEN      | 12000.0 \$/MAN-YR | .12    | 366             | .12         |
| ELECTRICITY   | .13 KWH/LB    | 1.0 CENTS/KWH     | .13    | 307             | .13         |
| STEAM   | 5.00 LB/LB    | 75.0 CENTS/LB     | .37    | 106             | .37         |
| WATER   | 8.00 GAL/LB   | 10.0 CENTS/GAL    | .08    | 906             | .08         |
| FUEL  | .01 GAL/LB    | 7.0 CENTS/GAL     | .10    | 280             | .10         |
| TOTAL (CENTS/LB)  |               |                   | 2.20   |                 | 1.32        |
| RAW MATERIAL COST (CENTS/LB)                                    |               |                   |        |                 |             |
| UREA  | 1.23200 LB/LB | 4.00 CENTS/LB     | 4.93   |                 | 4.93        |
| AMMONIUM NITRATE  | .65600 LB/LB  | 2.50 CENTS/LB     | 1.64   |                 | 1.64        |
| CATALYST  | .00100 LB/LB  | 150.00 CENTS/LB   | .15    | 280             | .15         |
| TOTAL (CENTS/LB)  |               |                   | 6.72   |                 | 6.72        |
| PLANT OVERHEAD (CENTS/LB)                                       |               |                   | .20    |                 | .20         |
| TOTAL MILL COST (CENTS/LB) EX. BY-PRODUCT CREDIT                |               |                   | 6.92   |                 | 8.24        |
| BY-PRODUCT CREDIT (CENTS/LB)                                    |               |                   |        |                 |             |
| AMMONIUM CARBAMATE  | .60000 LB/LB  | .00 CENTS/LB      | .00    |                 | .00         |
| TOTAL (CENTS/LB)  |               |                   | .00    |                 | .00         |
| TOTAL MILL COST (CENTS/LB) INC. BY-PRODUCT CREDIT               |               |                   | 6.92   |                 | 8.24        |
|   |               |                   |        | Fringe          | 1.68        |
|   |               |                   |        | Price 0% return | 9.92¢/lb    |
| * 10 YEAR PLANT LIFE, EXISTING SITE                             |               |                   |        |                 |             |
| 15 PCT INDIRECT   |               |                   |        |                 |             |
| ** PERCENT CHANGE NEEDED TO AFFECT RETURN BY 1 PERCENT DECREASE |               |                   |        |                 |             |

(1) 50% is maintenance material

RETURN CALCULATIONS

|                   |             |
|-------------------|-------------|
| PLANT INVESTMENT  | 3.30 MM \$  |
| OPERATING COST    | 1.32 MM \$  |
| RAW MATERIAL COST | 6.72 MM \$  |
| TOTAL COST        | 11.34 MM \$ |

|                  |                |
|------------------|----------------|
| PRICE PER LB     | 11.34 CENTS/LB |
| PRICE PER 20 PCT | 11.34 CENTS/LB |
| PRICE PER 30 PCT | 11.34 CENTS/LB |

# GUANIMINE NITRATE PROJECT PACKED BED TUBULAR REACTOR

## APPENDIX I-6. MATHEMATICAL REACTOR PRINTOUTS

### MAJORITY READS

BULK DENSITY = 7.37 GRAMS/IN. IN.  
VOID FRACTION = .437  
TUBE DIAMETER = 2.00 INCHES  
FEED TEMPERATURE = 190.0 C.  
JACKET TEMPERATURE = 195.0 C.  
OVERALL HEAT TRANSFER COEFFICIENT = 1.00 CAL./SQ. IN.-MIN.-C.

| DISTANCE<br>INCHES | MOLAR FLOW RATES<br>MOLES/MINUTE | MOLT<br>GAS | MOLE<br>AMMONIUM<br>NITRATE | FRACTIONS<br>H2O GUANIMINE<br>NITRATE | CONVERSION<br>% H2O REAC/<br>% H2O FEED | YIELD<br>M. GN/<br>% H2O REAC | TEMPERATURE<br>DEG. C. |
|--------------------|----------------------------------|-------------|-----------------------------|---------------------------------------|---|-------------------------------|------------------------|
| 0.00               | .415                             | .000        | .4750                       | .4750                                 | .0000                                   | .0000                         | 190.0                  |
| .500               | .412                             | .003        | .4746                       | .4666                                 | .0176                                   | .2865                         | 189.5                  |
| 1.000              | .409                             | .006        | .4741                       | .4643                                 | .0344                                   | .2873                         | 189.1                  |
| 1.500              | .405                             | .009        | .4735                       | .4601                                 | .0515                                   | .2883                         | 188.6                  |
| 2.000              | .402                             | .011        | .4729                       | .4560                                 | .0650                                   | .2906                         | 188.4                  |
| 2.500              | .399                             | .014        | .4722                       | .4520                                 | .0810                                   | .2920                         | 188.4                  |
| 3.000              | .396                             | .017        | .4715                       | .4483                                 | .1016                                   | .2984                         | 188.1                  |
| 3.500              | .393                             | .020        | .4708                       | .4449                                 | .1255                                   | .3040                         | 188.2                  |
| 4.000              | .391                             | .023        | .4701                       | .4416                                 | .1515                                   | .3115                         | 188.3                  |
| 4.500              | .388                             | .026        | .4694                       | .4385                                 | .1768                                   | .3143                         | 188.5                  |
| 5.000              | .385                             | .029        | .4687                       | .4353                                 | .2043                                   | .3252                         | 188.7                  |
| 5.500              | .382                             | .032        | .4680                       | .4322                                 | .2319                                   | .3323                         | 188.9                  |
| 6.000              | .379                             | .035        | .4673                       | .4291                                 | .2610                                   | .3407                         | 189.1                  |
| 6.500              | .376                             | .038        | .4666                       | .4260                                 | .2915                                   | .3463                         | 189.3                  |
| 7.000              | .373                             | .041        | .4659                       | .4229                                 | .3222                                   | .3542                         | 189.5                  |
| 7.500              | .370                             | .044        | .4652                       | .4198                                 | .3545                                   | .3615                         | 189.7                  |
| 8.000              | .367                             | .047        | .4645                       | .4167                                 | .3884                                   | .3690                         | 189.9                  |
| 8.500              | .364                             | .050        | .4638                       | .4136                                 | .4234                                   | .3753                         | 190.1                  |
| 9.000              | .361                             | .053        | .4631                       | .4105                                 | .4594                                   | .3836                         | 190.3                  |
| 9.500              | .358                             | .056        | .4624                       | .4074                                 | .4918                                   | .3905                         | 190.5                  |
| 10.000             | .355                             | .059        | .4617                       | .4043                                 | .5215                                   | .3979                         | 190.7                  |
| 10.500             | .352                             | .062        | .4610                       | .4012                                 | .5495                                   | .4040                         | 190.9                  |
| 11.000             | .349                             | .065        | .4603                       | .3981                                 | .5758                                   | .4115                         | 191.1                  |
| 11.500             | .346                             | .068        | .4596                       | .3950                                 | .6015                                   | .4186                         | 191.3                  |
| 12.000             | .343                             | .071        | .4589                       | .3919                                 | .6255                                   | .4259                         | 191.5                  |
| 12.500             | .340                             | .074        | .4582                       | .3888                                 | .6484                                   | .4329                         | 191.7                  |
| 13.000             | .337                             | .077        | .4575                       | .3857                                 | .6694                                   | .4399                         | 191.9                  |
| 13.500             | .334                             | .080        | .4568                       | .3826                                 | .6884                                   | .4469                         | 192.1                  |
| 14.000             | .331                             | .083        | .4561                       | .3795                                 | .7054                                   | .4539                         | 192.3                  |
| 14.500             | .328                             | .086        | .4554                       | .3764                                 | .7204                                   | .4609                         | 192.5                  |
| 15.000             | .325                             | .089        | .4547                       | .3733                                 | .7344                                   | .4679                         | 192.7                  |
| 15.500             | .322                             | .092        | .4540                       | .3702                                 | .7474                                   | .4749                         | 192.9                  |
| 16.000             | .319                             | .095        | .4533                       | .3671                                 | .7594                                   | .4819                         | 193.1                  |
| 16.500             | .316                             | .098        | .4526                       | .3640                                 | .7704                                   | .4889                         | 193.3                  |
| 17.000             | .313                             | .101        | .4519                       | .3609                                 | .7804                                   | .4959                         | 193.5                  |
| 17.500             | .310                             | .104        | .4512                       | .3578                                 | .7894                                   | .5029                         | 193.7                  |
| 18.000             | .307                             | .107        | .4505                       | .3547                                 | .7974                                   | .5099                         | 193.9                  |
| 18.500             | .304                             | .110        | .4498                       | .3516                                 | .8054                                   | .5169                         | 194.1                  |
| 19.000             | .301                             | .113        | .4491                       | .3485                                 | .8124                                   | .5239                         | 194.3                  |
| 19.500             | .298                             | .116        | .4484                       | .3454                                 | .8184                                   | .5309                         | 194.5                  |
| 20.000             | .295                             | .119        | .4477                       | .3423                                 | .8244                                   | .5379                         | 194.7                  |
| 20.500             | .292                             | .122        | .4470                       | .3392                                 | .8294                                   | .5449                         | 194.9                  |
| 21.000             | .289                             | .125        | .4463                       | .3361                                 | .8344                                   | .5519                         | 195.1                  |
| 21.500             | .286                             | .128        | .4456                       | .3330                                 | .8384                                   | .5589                         | 195.3                  |
| 22.000             | .283                             | .131        | .4449                       | .3299                                 | .8424                                   | .5659                         | 195.5                  |
| 22.500             | .280                             | .134        | .4442                       | .3268                                 | .8464                                   | .5729                         | 195.7                  |
| 23.000             | .277                             | .137        | .4435                       | .3237                                 | .8494                                   | .5799                         | 195.9                  |
| 23.500             | .274                             | .140        | .4428                       | .3206                                 | .8524                                   | .5869                         | 196.1                  |
| 24.000             | .271                             | .143        | .4421                       | .3175                                 | .8554                                   | .5939                         | 196.3                  |
| 24.500             | .268                             | .146        | .4414                       | .3144                                 | .8584                                   | .6009                         | 196.5                  |
| 25.000             | .265                             | .149        | .4407                       | .3113                                 | .8614                                   | .6079                         | 196.7                  |
| 25.500             | .262                             | .152        | .4400                       | .3082                                 | .8644                                   | .6149                         | 196.9                  |
| 26.000             | .259                             | .155        | .4393                       | .3051                                 | .8674                                   | .6219                         | 197.1                  |
| 26.500             | .256                             | .158        | .4386                       | .3020                                 | .8704                                   | .6289                         | 197.3                  |
| 27.000             | .253                             | .161        | .4379                       | .2989                                 | .8734                                   | .6359                         | 197.5                  |
| 27.500             | .250                             | .164        | .4372                       | .2958                                 | .8764                                   | .6429                         | 197.7                  |
| 28.000             | .247                             | .167        | .4365                       | .2927                                 | .8794                                   | .6499                         | 197.9                  |
| 28.500             | .244                             | .170        | .4358                       | .2896                                 | .8824                                   | .6569                         | 198.1                  |
| 29.000             | .241                             | .173        | .4351                       | .2865                                 | .8854                                   | .6639                         | 198.3                  |
| 29.500             | .238                             | .176        | .4344                       | .2834                                 | .8884                                   | .6709                         | 198.5                  |
| 30.000             | .235                             | .179        | .4337                       | .2803                                 | .8914                                   | .6779                         | 198.7                  |
| 30.500             | .232                             | .182        | .4330                       | .2772                                 | .8944                                   | .6849                         | 198.9                  |
| 31.000             | .229                             | .185        | .4323                       | .2741                                 | .8974                                   | .6919                         | 199.1                  |
| 31.500             | .226                             | .188        | .4316                       | .2710                                 | .9004                                   | .6989                         | 199.3                  |
| 32.000             | .223                             | .191        | .4309                       | .2679                                 | .9034                                   | .7059                         | 199.5                  |
| 32.500             | .220                             | .194        | .4302                       | .2648                                 | .9064                                   | .7129                         | 199.7                  |
| 33.000             | .217                             | .197        | .4295                       | .2617                                 | .9094                                   | .7199                         | 199.9                  |
| 33.500             | .214                             | .200        | .4288                       | .2586                                 | .9124                                   | .7269                         | 200.1                  |
| 34.000             | .211                             | .203        | .4281                       | .2555                                 | .9154                                   | .7339                         | 200.3                  |
| 34.500             | .208                             | .206        | .4274                       | .2524                                 | .9184                                   | .7409                         | 200.5                  |
| 35.000             | .205                             | .209        | .4267                       | .2493                                 | .9214                                   | .7479                         | 200.7                  |
| 35.500             | .202                             | .212        | .4260                       | .2462                                 | .9244                                   | .7549                         | 200.9                  |
| 36.000             | .200                             | .215        | .4253                       | .2431                                 | .9274                                   | .7619                         | 201.1                  |
| 36.500             | .197                             | .218        | .4246                       | .2400                                 | .9304                                   | .7689                         | 201.3                  |
| 37.000             | .194                             | .221        | .4239                       | .2369                                 | .9334                                   | .7759                         | 201.5                  |
| 37.500             | .191                             | .224        | .4232                       | .2338                                 | .9364                                   | .7829                         | 201.7                  |
| 38.000             | .188                             | .227        | .4225                       | .2307                                 | .9394                                   | .7899                         | 201.9                  |
| 38.500             | .185                             | .230        | .4218                       | .2276                                 | .9424                                   | .7969                         | 202.1                  |
| 39.000             | .182                             | .233        | .4211                       | .2245                                 | .9454                                   | .8039                         | 202.3                  |
| 39.500             | .180                             | .236        | .4204                       | .2214                                 | .9484                                   | .8109                         | 202.5                  |
| 40.000             | .177                             | .239        | .4197                       | .2183                                 | .9514                                   | .8179                         | 202.7                  |

MELT FEED RATE = 4.00 LB./HR.  
FEED WEIGHT FRACTIONS = AMMONIUM NITRATE = .5197  
H2O = .4803  
GUANIMINE NITRATE = .0004  
PRODUCT RATE = 5.157 LB./HR.  
PRODUCT WEIGHT FRACTIONS = AMMONIUM NITRATE = .4484  
H2O = .5116  
GUANIMINE NITRATE = .0374  
TOTAL CATALYST WEIGHT = 1111.37 GRAMS  
MINIMAL RESIDENCE TIME = 32.62 MINUTES  
DATE CONSTANT FOR GM  
FREQUENCY FACTOR = .1411E 13  
ACTIVATION ENERGY/R = .1656E 05  
RATE CONSTANT FOR H2O DECOMPOSITION  
FREQUENCY FACTOR = .2000E 14  
ACTIVATION ENERGY/R = .1650E 05

GUANIDINE NITRATE PROJECT  
PACKED BED TUBULAR REACTOR

MOUDRY BEADS

BULK DENSITY = 7.37 GRAMS/CC. IN.

VOID FRACTION = .437

TUBE DIAMETER = 2.00 INCHES

FEED TEMPERATURE = 190.0 C.

JACKET TEMPERATURE = 195.0 C.

OVERALL HEAT TRANSFER COEFFICIENT = 1.08 CAL./SQ.IN.-MIN.-C.

| DISTANCE<br>INCHES | MOLAR FLOW RATES<br>MOLES/MINUTE<br>MELT | GAS  | AMMONIUM<br>NITRATE | MOLE<br>NITRATE | FRACTIONS<br>UREA<br>GUANIDINE<br>NITRATE | CONVERSION<br>M. U. REAC/<br>M. U. FEED | YIELD<br>M. GN/<br>% U. REAC | TEMPERATURE<br>DEG. C. |
|--------------------|--|------|---------------------|-----------------|---|---|------------------------------|------------------------|
| .000               | .831                                     | .000 | .4730               | .4730           | .4730                                     | .0000                                   | .0000                        | 190.0                  |
| .500               | .827                                     | .003 | .4734               | .4734           | .4708                                     | .0089                                   | .2858                        | 189.7                  |
| 1.000              | .824                                     | .006 | .4746               | .4746           | .4686                                     | .0174                                   | .2865                        | 189.4                  |
| 1.500              | .820                                     | .009 | .4753               | .4753           | .4664                                     | .0251                                   | .2872                        | 189.3                  |
| 2.000              | .817                                     | .012 | .4761               | .4761           | .4643                                     | .0344                                   | .2879                        | 189.1                  |
| 2.500              | .814                                     | .014 | .4768               | .4768           | .4622                                     | .0425                                   | .2886                        | 188.9                  |
| 3.000              | .799                                     | .028 | .4802               | .4802           | .4520                                     | .0810                                   | .2920                        | 188.4                  |
| 3.500              | .785                                     | .041 | .4834               | .4834           | .4421                                     | .1172                                   | .2952                        | 188.2                  |
| 4.000              | .771                                     | .053 | .4865               | .4865           | .4323                                     | .1516                                   | .2984                        | 188.1                  |
| 4.500              | .758                                     | .066 | .4894               | .4894           | .4226                                     | .1847                                   | .3016                        | 188.2                  |
| 5.000              | .746                                     | .078 | .4922               | .4922           | .4120                                     | .2155                                   | .3049                        | 188.2                  |
| 5.500              | .734                                     | .090 | .4948               | .4948           | .4032                                     | .2472                                   | .3082                        | 188.3                  |
| 6.000              | .722                                     | .102 | .4973               | .4973           | .3936                                     | .2756                                   | .3115                        | 188.3                  |
| 6.500              | .711                                     | .113 | .4997               | .4997           | .3841                                     | .3052                                   | .3149                        | 188.4                  |
| 7.000              | .700                                     | .125 | .5019               | .5019           | .3746                                     | .3326                                   | .3183                        | 188.5                  |
| 7.500              | .690                                     | .136 | .5039               | .5039           | .3652                                     | .3590                                   | .3217                        | 188.6                  |
| 8.000              | .680                                     | .147 | .5058               | .5058           | .3559                                     | .3843                                   | .3252                        | 188.7                  |
| 8.500              | .670                                     | .158 | .5076               | .5076           | .3467                                     | .4086                                   | .3286                        | 188.8                  |
| 9.000              | .661                                     | .169 | .5091               | .5091           | .3377                                     | .4319                                   | .3323                        | 188.9                  |
| 9.500              | .652                                     | .180 | .5105               | .5105           | .3288                                     | .4543                                   | .3359                        | 189.0                  |
| 10.000             | .644                                     | .190 | .5117               | .5117           | .3200                                     | .4756                                   | .3395                        | 189.1                  |
| 10.500             | .636                                     | .201 | .5128               | .5128           | .3114                                     | .4951                                   | .3432                        | 189.2                  |
| 11.000             | .628                                     | .211 | .5137               | .5137           | .3030                                     | .5157                                   | .3468                        | 189.3                  |
| 11.500             | .621                                     | .221 | .5144               | .5144           | .2947                                     | .5366                                   | .3505                        | 189.4                  |
| 12.000             | .619                                     | .223 | .5146               | .5146           | .2931                                     | .5580                                   | .3542                        | 189.4                  |

MELT FEED RATE = 8.00 LB./HR.

FEED WEIGHT FRACTIONS = AMMONIUM NITRATE = .5107

UREA = .3808

GUANIDINE NITRATE = .0005

PRODUCT RATE = 6.735 LB./HR.

PRODUCT WEIGHT FRACTIONS = AMMONIUM NITRATE = .5007

UREA = .2139

GUANIDINE NITRATE = .2854

TOTAL CATALYST WEIGHT = 111.37 GRAMS

NOMINAL RESIDENCE TIME = 46.31 MINUTES

RATE CONSTANT FOR GN

FREQUENCY FACTOR = .131E 13

ACTIVATION ENERGY/R = .165E 05

RATE CONSTANT FOR UREA DECOMPOSITION

FREQUENCY FACTOR = .200E 14

ACTIVATION ENERGY/R = .168E 05

GUANIDINE NITRATE PROJECT  
PACKED BED TUBULAR REACTOR

MOISTURE BEADS

SULK DENSITY = 7.37 GRAMS/CC. IN.  
VOID FRACTION = .437  
TUBE DIAMETER = 2.00 INCHES  
FEED TEMPERATURE = 100.0 C.  
JACKET TEMPERATURE = 105.0 C.  
OVERALL HEAT TRANSFER COEFFICIENT = 1.04 CAL./SQ. IN.-MIN.-C.

| DISTANCE<br>INCHES | MOLAR FLOW RATES<br>MOLES/MINUTE | MOLE<br>AMMONIUM<br>NITRATE | FRACTIONS<br>UREA GUANIDINE<br>NITRATE | CONVERSION<br>% U REAC/<br>% U FED | YIELD<br>M. GN/<br>% U REAC | TEMPERATURE<br>DEG. C. |
|--------------------|----------------------------------|-----------------------------|--|------------------------------------|-----------------------------|------------------------|
| 0.00               | .432                             | .5000                       | .5000                                  | .0000                              | .0000                       | 190.0                  |
| .500               | .428                             | .5022                       | .4952                                  | .0150                              | .2711                       | 189.3                  |
| 1.000              | .424                             | .5042                       | .4907                                  | .0356                              | .2725                       | 188.8                  |
| 1.500              | .420                             | .5062                       | .4862                                  | .0535                              | .2738                       | 188.5                  |
| 2.000              | .417                             | .5081                       | .4819                                  | .0694                              | .2751                       | 188.2                  |
| 2.500              | .414                             | .5100                       | .4776                                  | .0856                              | .2763                       | 188.0                  |
| 3.000              | .408                             | .5118                       | .4734                                  | .1024                              | .2824                       | 187.6                  |
| 3.500              | .403                             | .5270                       | .4668                                  | .1124                              | .2886                       | 187.6                  |
| 4.000              | .398                             | .5347                       | .4561                                  | .1265                              | .2949                       | 187.8                  |
| 4.500              | .393                             | .5417                       | .4455                                  | .1432                              | .3015                       | 187.0                  |
| 5.000              | .387                             | .5481                       | .4340                                  | .1624                              | .3082                       | 186.5                  |
| 5.500              | .382                             | .5534                       | .4215                                  | .1830                              | .3151                       | 186.5                  |
| 6.000              | .375                             | .5587                       | .4080                                  | .2054                              | .3222                       | 186.5                  |
| 6.500              | .368                             | .5624                       | .3930                                  | .2294                              | .3294                       | 186.7                  |
| 7.000              | .361                             | .5661                       | .3760                                  | .2559                              | .3366                       | 186.5                  |
| 7.500              | .354                             | .5685                       | .3580                                  | .2834                              | .3440                       | 186.0                  |
| 8.000              | .347                             | .5702                       | .3390                                  | .3124                              | .3514                       | 185.2                  |
| 8.500              | .340                             | .5711                       | .3190                                  | .3424                              | .3587                       | 184.4                  |
| 9.000              | .332                             | .5713                       | .2980                                  | .3734                              | .3661                       | 184.0                  |
| 9.500              | .325                             | .5709                       | .2760                                  | .4054                              | .3734                       | 183.1                  |
| 10.000             | .317                             | .5699                       | .2530                                  | .4384                              | .3804                       | 182.5                  |
| 10.500             | .309                             | .5684                       | .2290                                  | .4724                              | .3876                       | 182.5                  |
| 11.000             | .301                             | .5665                       | .2040                                  | .5074                              | .3946                       | 182.7                  |
| 11.500             | .293                             | .5642                       | .1780                                  | .5434                              | .4014                       | 182.4                  |
| 12.000             | .285                             | .5617                       | .1510                                  | .5804                              | .4086                       | 182.0                  |

MELT FEED RATE = 4.00 LB./HR.

FEED WEIGHT FRACTIONS = AMMONIUM NITRATE = .5714  
UREA = .4286

PRODUCT RATE = 3.025 LB./HR.

PRODUCT WEIGHT FRACTIONS = AMMONIUM NITRATE = .5146  
UREA = .4854

TOTAL CATALYST WEIGHT = 111.57 GRAMS  
MINIMAL RESIDENCE TIME = 40.05 MINUTES  
RATE CONSTANT FOR RN

FREQUENCY FACTOR = .1311E 13  
ACTIVATION ENERGY/R = .1651E 05

RATE CONSTANT FOR UREA DECOMPOSITION  
FREQUENCY FACTOR = .2004E 14  
ACTIVATION ENERGY/R = .1600E 05



GUANIDINE NITRATE PROJECT  
PACKED BED TUBULAR REACTOR

MOISTURE BEADS

BULK DENSITY = 7.37 GRAMS/CC. IN.  
VOID FRACTION = .437  
TUBE DIAMETER = 2.00 INCHES  
FEED TEMPERATURE = 190.0 C.  
JACKET TEMPERATURE = 195.0 C.  
OVERALL HEAT TRANSFER COEFFICIENT = 1.00 CAL./SQ. IN.-MIN.-C.

| DISTANCE<br>INCHES | MOLAR FLOW RATES<br>MOLES/MINUTE | MOLT<br>GAS | AMMONIUM<br>NITRATE | FRACTIONS<br>UREA GUANIDINE<br>NITRATE | CONVERSION<br>MOL REACT/<br>MOL FEED | YIELD<br>MOL GN/<br>MOL FEED | TEMPERATURE<br>HFG. C. |
|--------------------|----------------------------------|-------------|---------------------|--|--------------------------------------|------------------------------|------------------------|
| .000               | .634                             | .000        | .5000               | .5000                                  | .0000                                | .0000                        | 190.0                  |
| .500               | .644                             | .003        | .5215               | .4964                                  | .0127                                | .2706                        | 189.5                  |
| 1.000              | .640                             | .007        | .5020               | .4937                                  | .0240                                | .2716                        | 189.2                  |
| 1.500              | .636                             | .010        | .5042               | .4907                                  | .0356                                | .2725                        | 188.8                  |
| 2.000              | .632                             | .013        | .5056               | .4877                                  | .0480                                | .2734                        | 188.6                  |
| 2.500              | .629                             | .016        | .5069               | .4848                                  | .0590                                | .2742                        | 188.4                  |
| 3.000              | .612                             | .030        | .5184               | .4706                                  | .1102                                | .2784                        | 187.8                  |
| 7.500              | .596                             | .044        | .5184               | .4564                                  | .1530                                | .2824                        | 187.6                  |
| 10.000             | .582                             | .057        | .5243               | .4430                                  | .2046                                | .2865                        | 187.6                  |
| 12.500             | .566                             | .070        | .5206               | .4293                                  | .2470                                | .2907                        | 187.7                  |
| 15.000             | .554                             | .083        | .5347               | .4155                                  | .2892                                | .2949                        | 187.8                  |
| 17.500             | .542                             | .094        | .5304               | .4017                                  | .3285                                | .2993                        | 187.9                  |
| 20.000             | .529                             | .108        | .5430               | .3881                                  | .3658                                | .3037                        | 188.0                  |
| 22.500             | .518                             | .120        | .5481               | .3745                                  | .4012                                | .3082                        | 188.1                  |
| 25.000             | .507                             | .132        | .5520               | .3611                                  | .4344                                | .3124                        | 188.2                  |
| 27.500             | .497                             | .144        | .5555               | .3479                                  | .4655                                | .3174                        | 188.4                  |
| 30.000             | .487                             | .154        | .5587               | .3340                                  | .4964                                | .3222                        | 188.5                  |
| 32.500             | .478                             | .167        | .5615               | .3222                                  | .5236                                | .3260                        | 188.7                  |
| 35.000             | .469                             | .178        | .5640               | .3070                                  | .5510                                | .3314                        | 188.8                  |
| 37.500             | .461                             | .188        | .5663               | .2924                                  | .5750                                | .3366                        | 189.0                  |
| 40.000             | .454                             | .199        | .5674               | .2861                                  | .5992                                | .3415                        | 189.1                  |
| 42.500             | .447                             | .209        | .5691               | .2744                                  | .6210                                | .3465                        | 189.3                  |
| 45.000             | .440                             | .219        | .5702               | .2640                                  | .6414                                | .3514                        | 189.4                  |
| 47.500             | .434                             | .229        | .5700               | .2535                                  | .6605                                | .3563                        | 189.6                  |
| 49.000             | .433                             | .231        | .5710               | .2514                                  | .6641                                | .3573                        | 189.6                  |

MELT FEED RATE = 4.00 LBS./HR.  
FEED WEIGHT FRACTIONS = AMMONIUM NITRATE = .5714  
UREA = .4286  
QUANTITIES NITRATE = .0000  
PRODUCT RATE = 4.210 LBS./HR.  
PRODUCT WEIGHT FRACTIONS = AMMONIUM NITRATE = .5541  
UREA = .4459  
QUANTITIES NITRATE = .2629  
TOTAL CATALYST WEIGHT = 1111.37 GRAMS  
NOMINAL RESIDENCE TIME = 50.37 MINUTES  
RATE CONSTANT FOR GN  
FREQUENCY FACTOR = .1311E 13  
ACTIVATION ENERGY = .1455E 05  
RATE CONSTANT FOR UREA DECOMPOSITION  
FREQUENCY FACTOR = .2004E 12  
ACTIVATION ENERGY = .1480E 05

GUANIDINE NITRATE PROJECT  
PACKED BED TUBULAR REACTOR

MOUDRY BEADS

BULK DENSITY = 7.37 GRAMS/CC. IN.  
VOID FRACTION = .437  
TUBE DIAMETER = 2.00 INCHES  
FEED TEMPERATURE = 190.0 C.  
JACKET TEMPERATURE = 195.0 C.  
OVERALL HEAT TRANSFER COEFFICIENT = 1.02 CAL./SQ. IN. - MIN. - C.

| DISTANCE<br>INCHES | MOLAR FLOW RATE<br>MOLES/MINUTE<br>MELT | MOLAR FLOW RATE<br>GAS | AMMONIUM<br>NITRATE | FRACTIONS<br>UPFA GUANIDINE<br>NITRATE | CONVERSION<br>M.O. REAC/<br>M.O. FEED | YIELD<br>M. GN/<br>M.O. FEED | TEMPERATURE<br>DEG. C. |
|--------------------|---|------------------------|---------------------|--|---------------------------------------|------------------------------|------------------------|
| .000               | .264                                    | .000                   | .5000               | .5000                                  | .0000                                 | .0000                        | 190.0                  |
| .500               | .860                                    | .003                   | .5011               | .4976                                  | .0096                                 | .2704                        | 189.6                  |
| 1.000              | .856                                    | .007                   | .5022               | .4952                                  | .0150                                 | .2711                        | 189.5                  |
| 1.500              | .852                                    | .010                   | .5032               | .4920                                  | .0270                                 | .2718                        | 189.1                  |
| 2.000              | .848                                    | .013                   | .5042               | .4907                                  | .0356                                 | .2725                        | 188.4                  |
| 2.500              | .844                                    | .016                   | .5052               | .4884                                  | .0452                                 | .2731                        | 188.6                  |
| 3.000              | .827                                    | .031                   | .5100               | .4776                                  | .0856                                 | .2763                        | 188.0                  |
| 3.500              | .811                                    | .045                   | .5145               | .4672                                  | .1232                                 | .2794                        | 187.7                  |
| 4.000              | .795                                    | .058                   | .5188               | .4568                                  | .1590                                 | .2824                        | 187.6                  |
| 4.500              | .780                                    | .072                   | .5230               | .4465                                  | .1934                                 | .2855                        | 187.6                  |
| 5.000              | .766                                    | .085                   | .5270               | .4361                                  | .2255                                 | .2885                        | 187.5                  |
| 5.500              | .752                                    | .098                   | .5309               | .4258                                  | .2584                                 | .2917                        | 187.7                  |
| 6.000              | .739                                    | .111                   | .5347               | .4155                                  | .2922                                 | .2946                        | 187.8                  |
| 6.500              | .726                                    | .123                   | .5383               | .4052                                  | .3188                                 | .2982                        | 187.9                  |
| 7.000              | .714                                    | .136                   | .5417               | .3949                                  | .3474                                 | .3015                        | 187.7                  |
| 7.500              | .702                                    | .148                   | .5450               | .3847                                  | .3748                                 | .3048                        | 188.0                  |
| 8.000              | .691                                    | .160                   | .5481               | .3745                                  | .4012                                 | .3082                        | 188.1                  |
| 8.500              | .680                                    | .172                   | .5511               | .3643                                  | .4256                                 | .3116                        | 188.2                  |
| 9.000              | .669                                    | .184                   | .5534               | .3545                                  | .4500                                 | .3151                        | 188.3                  |
| 9.500              | .659                                    | .196                   | .5564               | .3446                                  | .4741                                 | .3186                        | 188.4                  |
| 10.000             | .650                                    | .207                   | .5587               | .3340                                  | .4954                                 | .3222                        | 188.5                  |
| 10.500             | .640                                    | .219                   | .5609               | .3254                                  | .5177                                 | .3257                        | 188.6                  |
| 11.000             | .632                                    | .230                   | .5628               | .3160                                  | .5380                                 | .3294                        | 188.7                  |
| 11.500             | .623                                    | .241                   | .5645               | .3068                                  | .5574                                 | .3330                        | 188.8                  |
| 12.000             | .622                                    | .243                   | .5664               | .3050                                  | .5612                                 | .3337                        | 188.9                  |

FEED RATE = 8.00 LB./HR.  
FEED WEIGHT FRACTIONS = AMMONIUM NITRATE = .5714  
UPFA = .4286  
GUANIDINE NITRATE = .0000  
PRODUCT RATE = 6.525 LB./HR.  
PRODUCT WEIGHT FRACTIONS = AMMONIUM NITRATE = .5694  
UPFA = .2306  
GUANIDINE NITRATE = .2001  
TOTAL CATALYST WEIGHT = 1111.37 GRAMS  
NOMINAL RESIDENCE TIME = 44.52 MINUTES  
RATE CONSTANT FOR GN  
FREQUENCY FACTOR = .1311E 13  
ACTIVATION ENERGY/R = .1655E 05  
RATE CONSTANT FOR UPFA DECOMPOSITION  
FREQUENCY FACTOR = .2000E 14  
ACTIVATION ENERGY/R = .1680E 05

APPENDIX II

PHASE III, PART 1

GUANIDINE NITRATE PILOT PLANT OPERATIONS



Plant H-1, Candine Sitrato P11 & Plant

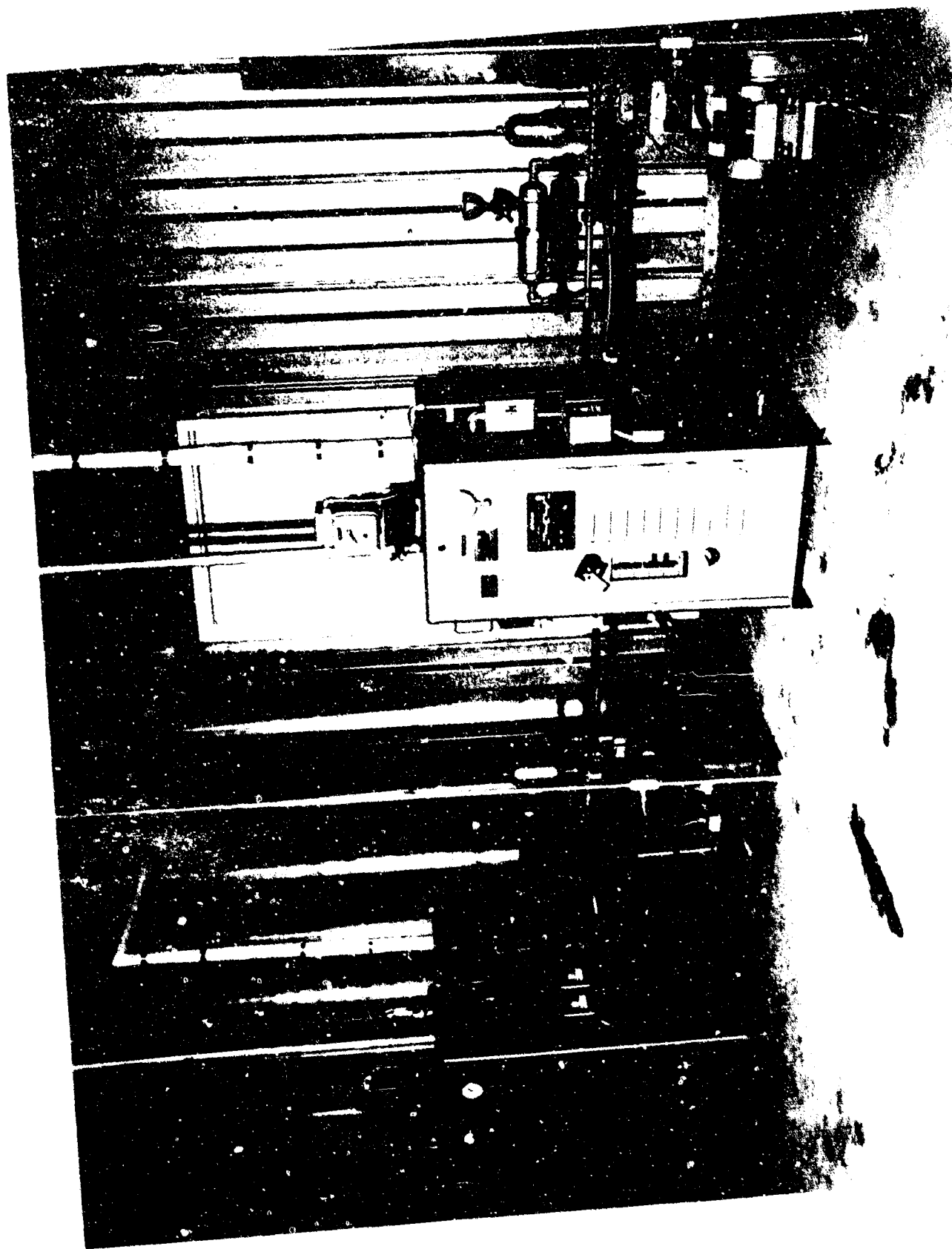


FIGURE II-2. High Pressure Steam Boilers

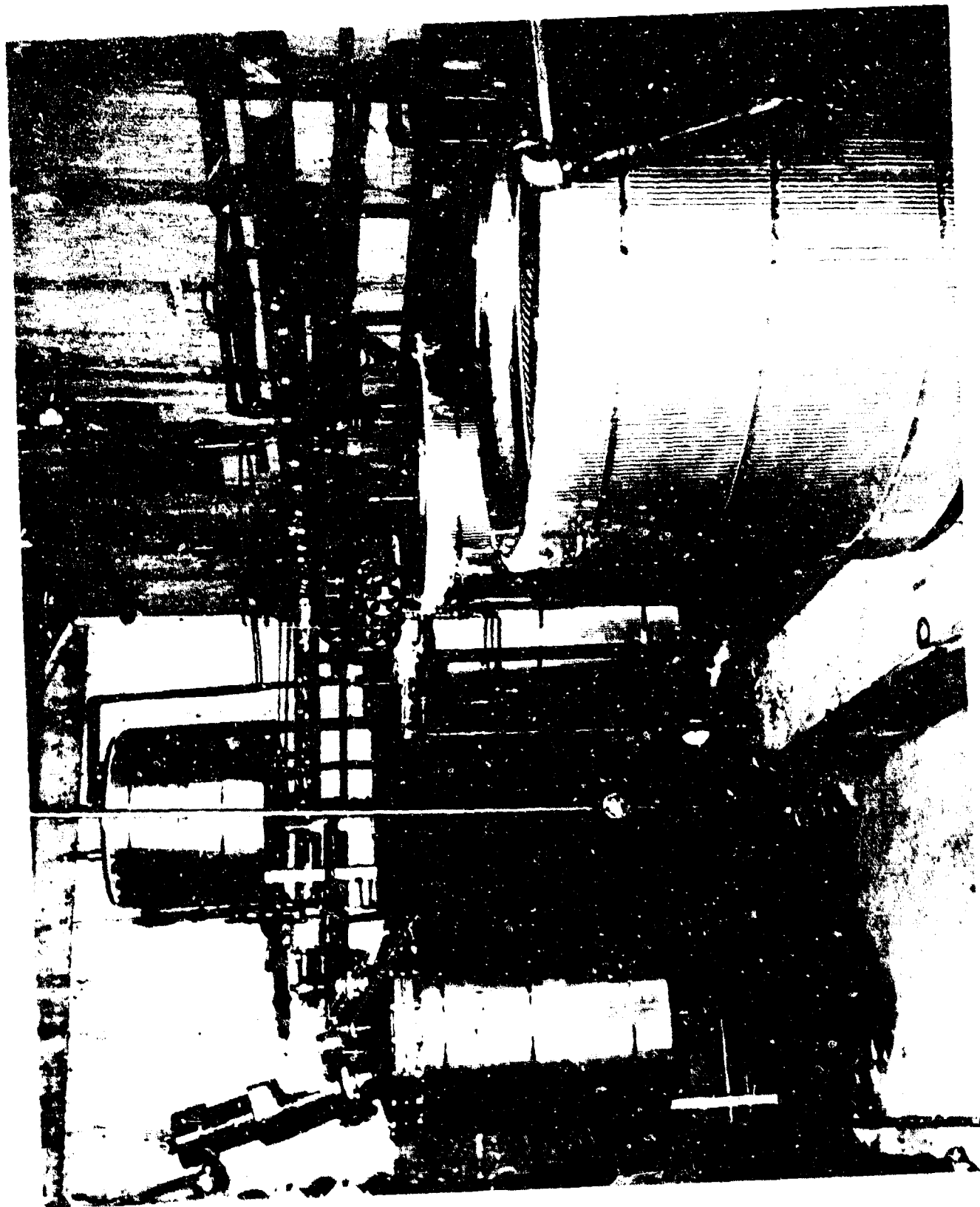


Figure 11-1. Operations in Nitrate Melt and Feed Systems

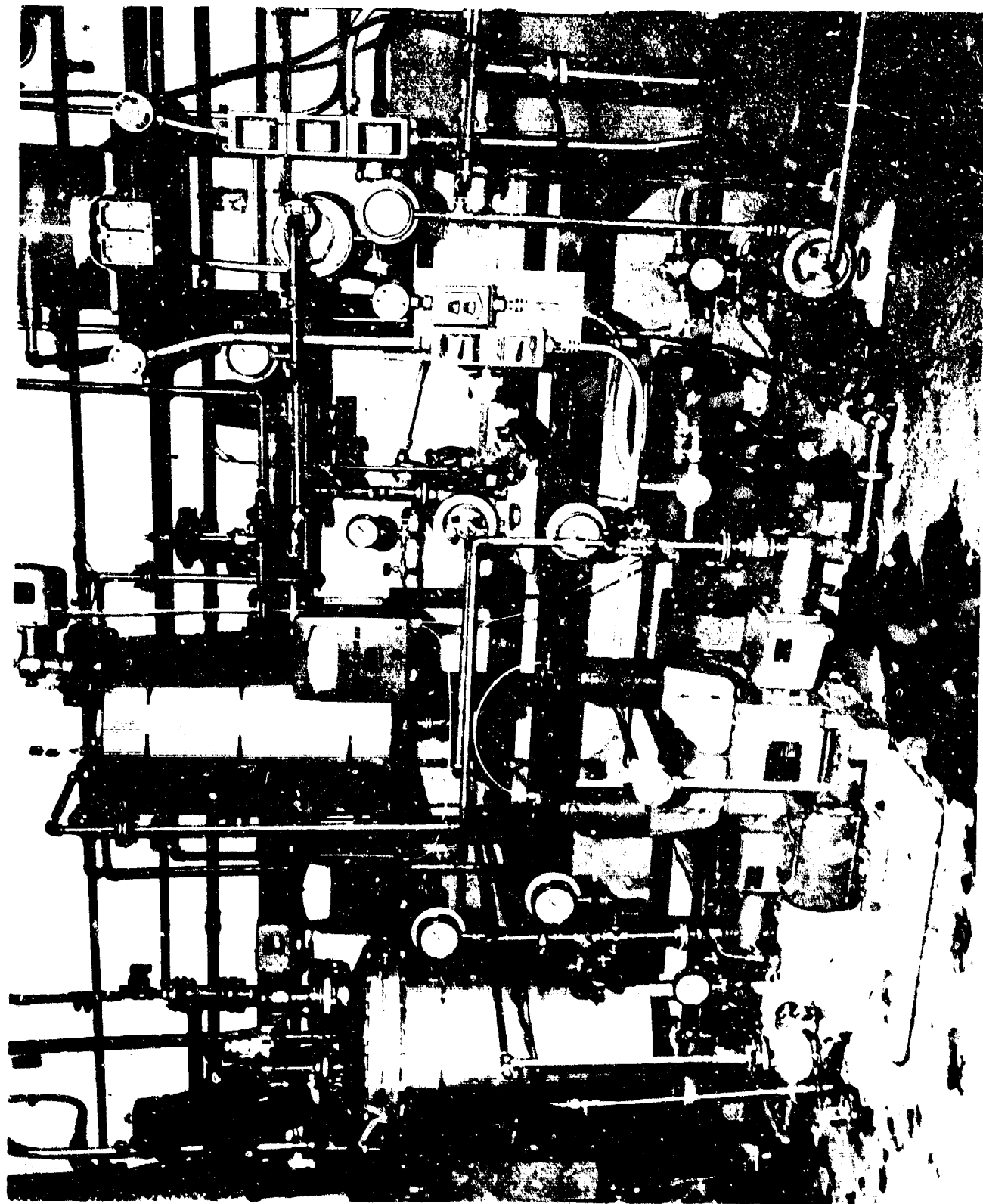


Figure 17-4 Urea Chloride Nitrate Feed System

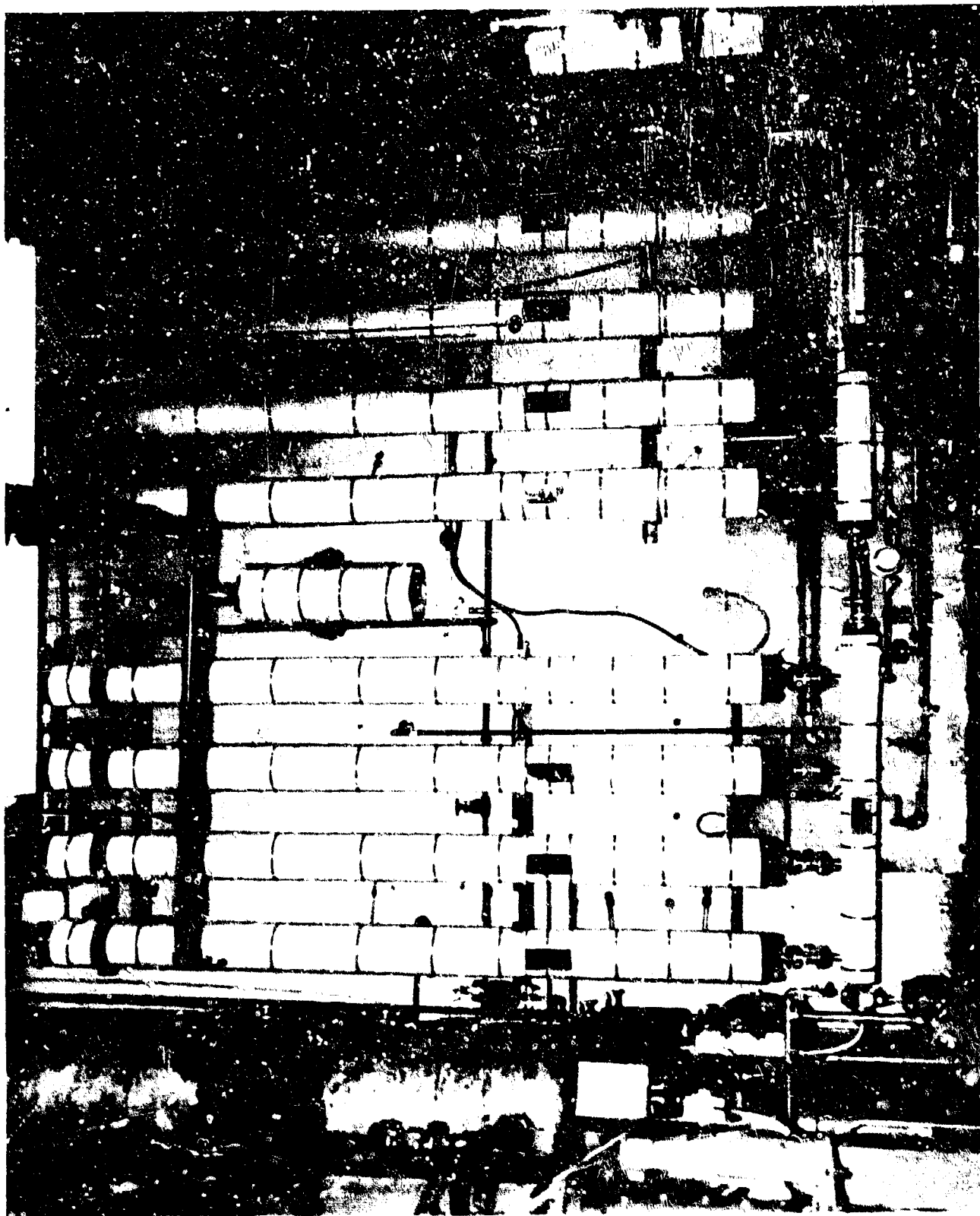


Figure II-5. Guanidine Nitrate Catalytic Tubular Reactors



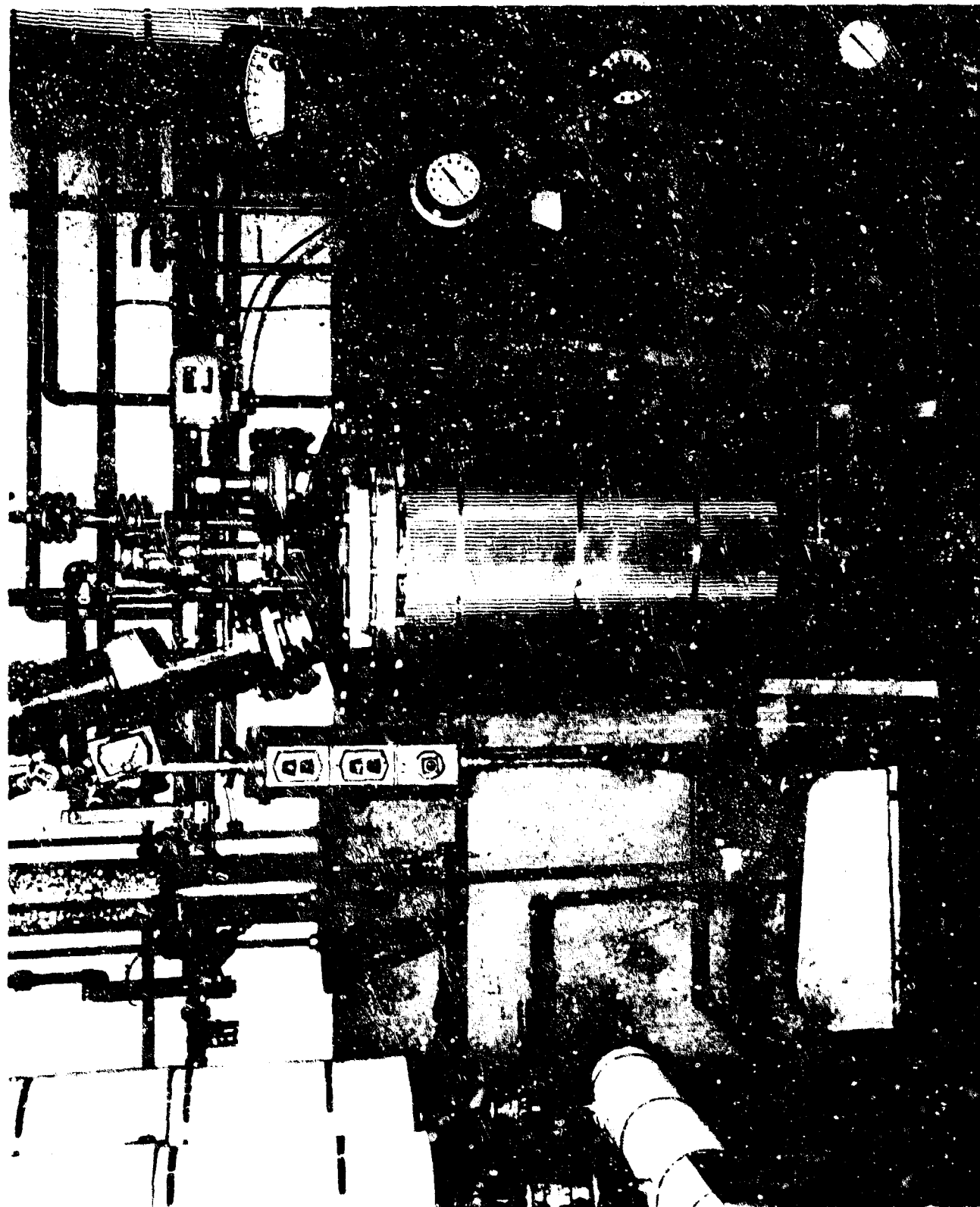


Figure II-6. Reactor Product Aqueous Quench Tank

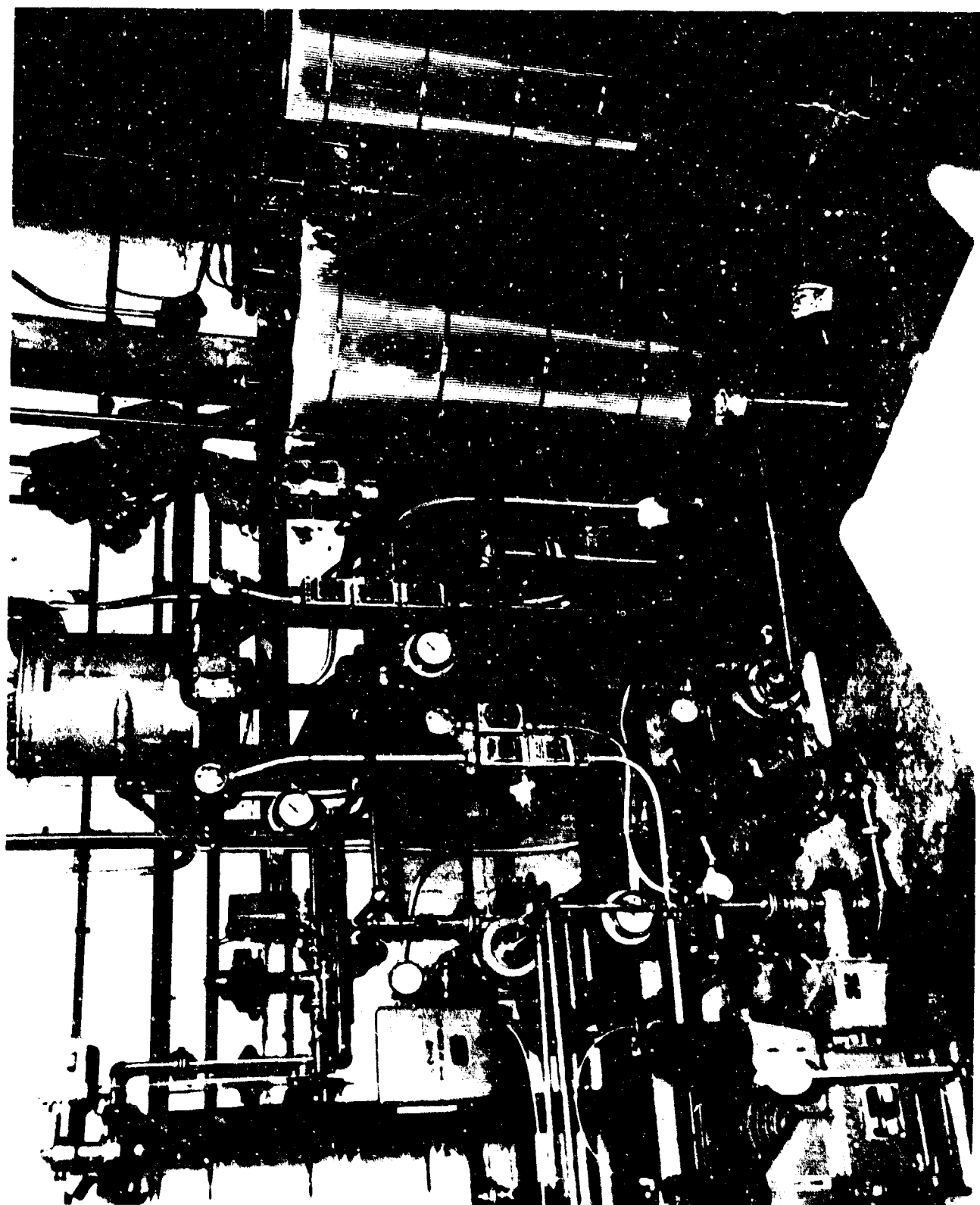


Figure 11-7. Vaporizer, Cryogenic and Evaporator Cold Tanks

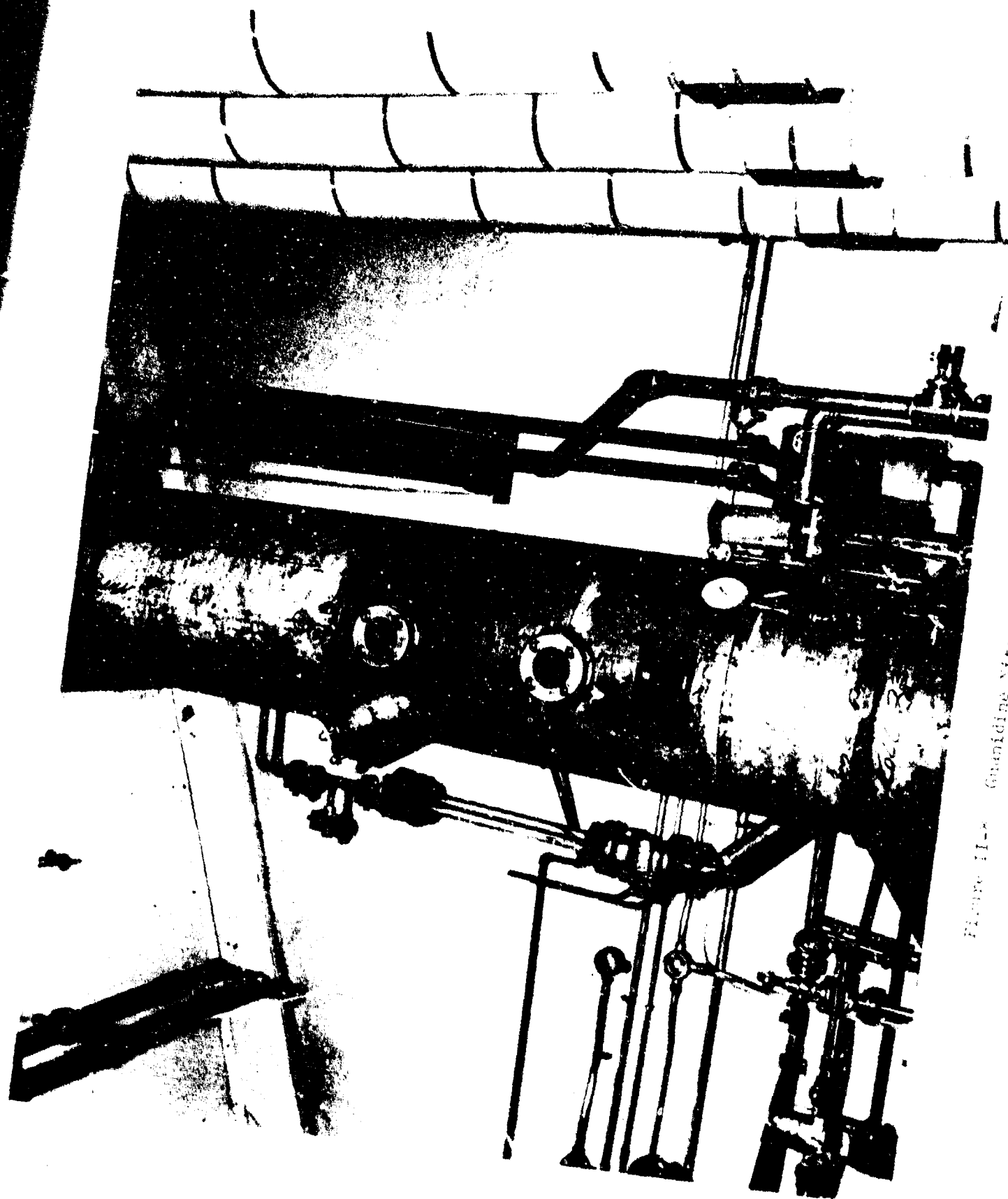


Figure 11-2 Guandine Nitrate Vacuum Crystallizer

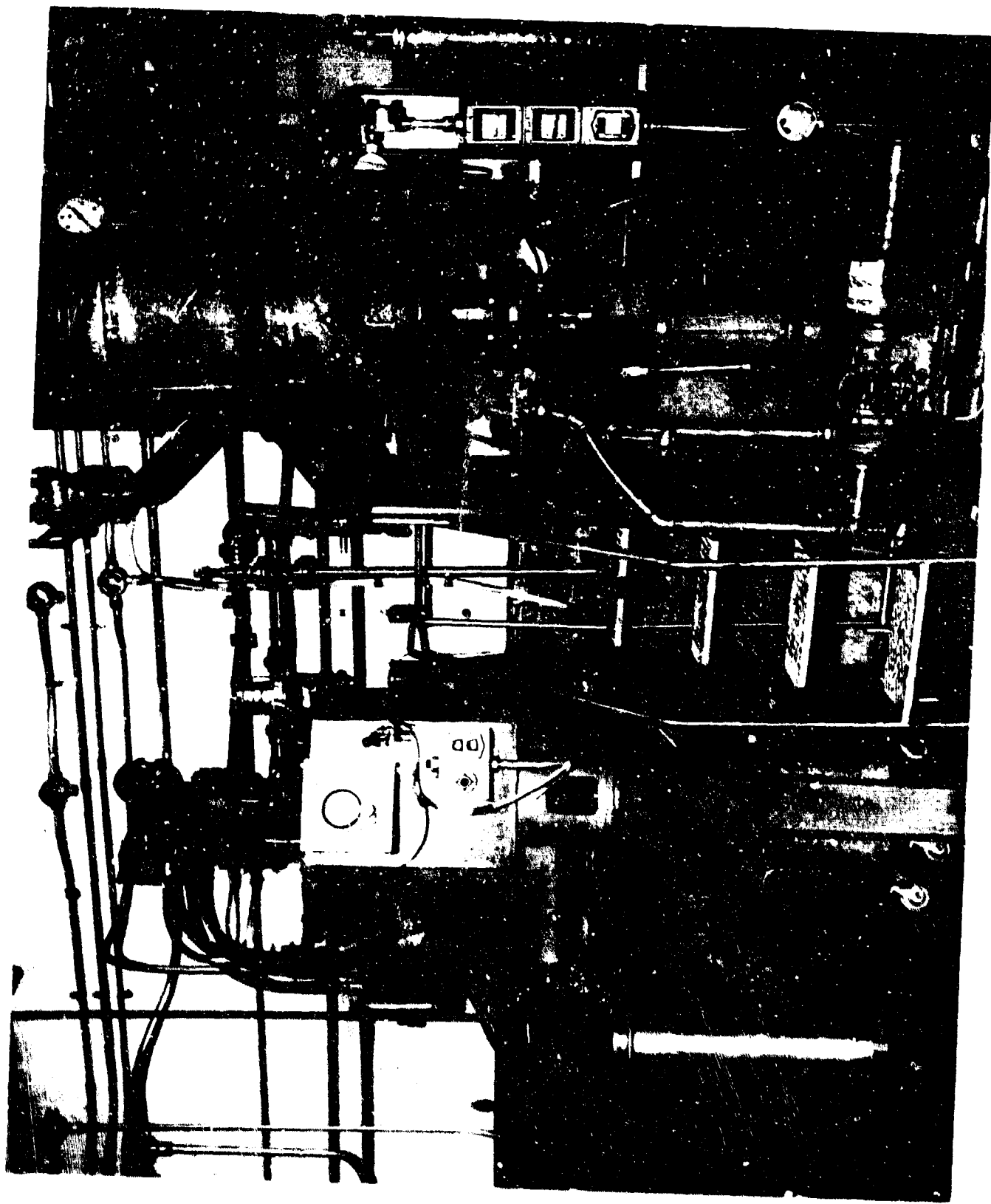


Figure 11-7 Perchloric Nitrate Crystallizer and Basket Centrifuge

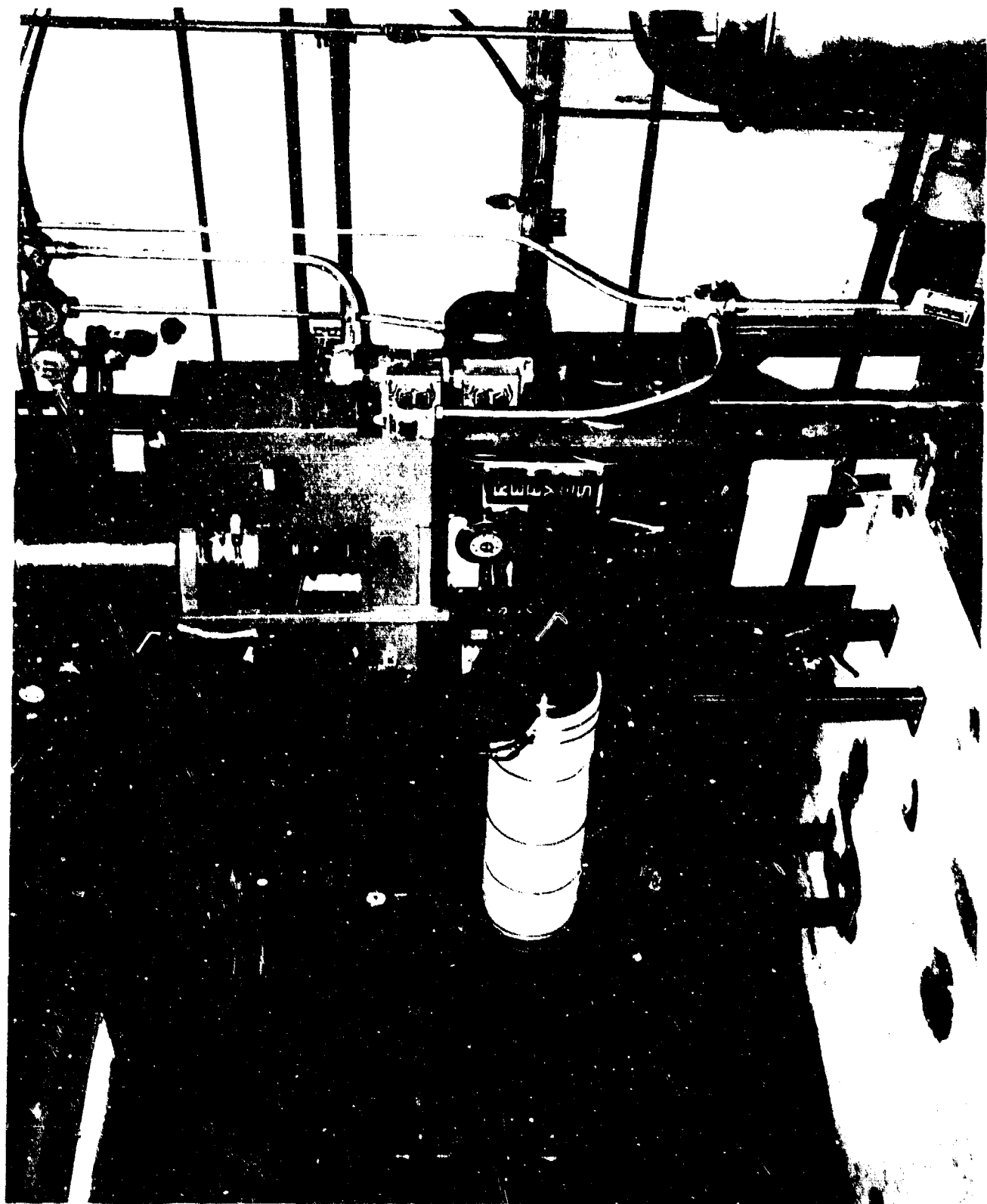


Figure II-19 Guandine Nitrate Drying System

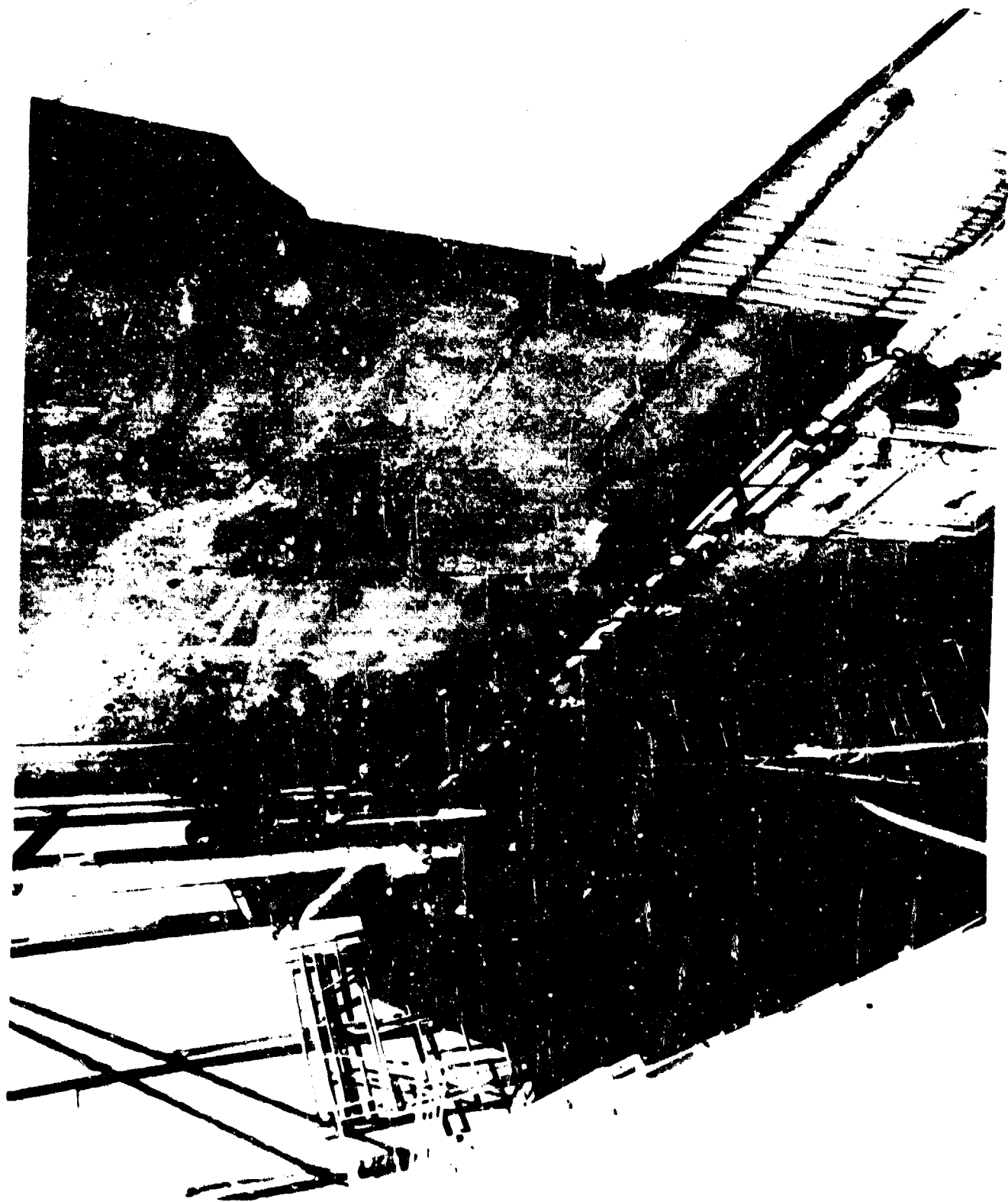


Figure 1. The building is a large structure for storing feed. It is located in the center of the farm.

TABLE II-1  
 REACTOR PERFORMANCE  
 (Operating Conditions and Calculated Results)

|                                   |                       | Run No. 1 (6/8/72 → 6/29/72) |           |           |           |           |           |           |           |           |           |           |           |
|-----------------------------------|-----------------------|------------------------------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
| Date                              |                       | 6/8                          | 6/13      | 6/14      | 6/15      | 6/15      | 6/16      | 6/21      | 6/21      | 6/21      | 6/21      | 6/21      | 6/22      |
| Sample No.                        | Calculations Based On | S1                           | S2        | S1        | S1        | S2        | S1        | S1        | S2        | S3        | S4        | S5        | S6        |
| Time                              |                       | 0200                         | 2020      | 0440      | 1620      | 2200      | 0400      | 0100      | 0400      | 0800      | 1300      | 1800      | 2015      |
| Data                              |                       |                              |           |           |           |           |           |           |           |           |           |           |           |
| Reactor Steam Pressure, psig      |                       | 170                          | 163       | 160       | 160       | 192       | 190       | 190       | 170/190   | 190       | 200       | 200       | 190       |
| Effective No. of Tubes            |                       | 2                            | 3         | 2         | 2         | 4         | 2         | 3         | 1-3       | 3         | 2         | 1-2       | 2         |
| 2 H <sub>2</sub> Feed/Product     |                       | 28.7/16.9                    | 41.5/25.6 | 39.8/29.3 | 28.7/20.6 | 28.2/14.3 | 56.1/40.0 | 43.4/19.6 | 42.6/25.3 | 43.1/24.7 | 36.7/22.5 | 39.3/21.0 | 34.8/24.3 |
| 2 AM <sub>2</sub> Feed/Product    |                       | 61.4/60.4                    | 54.0/55.8 | 52.9/53.8 | 53.4/57.6 | 53.7/52.8 | 36.9/35.6 | 50.2/41.6 | 50.1/44.1 | 52.7/46.2 | 50.1/54.8 | 55.6/53.2 | 57.3/60.5 |
| 2 CM <sub>2</sub> Feed/Product    |                       | 8.0/22.0                     | 1.2/13.9  | 6.2/11.1  | 11.3/14.6 | 12.7/31.1 | 3.2/12.9  | 5.5/35.1  | 3.5/27.8  | 4.8/24.6  | 4.2/22.1  | 2.4/14.9  | 6.0/13.7  |
| 2 Insolubles, Product             |                       | 0.35                         | Trace     | 0         | 0.4       | 1.3       | 0.25      | 0.19      | 0.62      | 0.41      | 0.29      | 0.15      | 0.19      |
| Feed Rate, lb/hr                  |                       | 50                           | 90        | 90        | 65        | 65        | 63        | 90        | 90        | 90        | 90        | 90        | 90        |
| Calculations                      |                       |                              |           |           |           |           |           |           |           |           |           |           |           |
| AM <sub>2</sub> to Mole Ratio     |                       | 1.6                          | 0.96      | 1.7       | 1.00      | 1.43      | 0.50      | 0.87      | 0.882     | 0.916     | 1.19      | 1.06      | 1.23      |
| CM <sub>2</sub> to Mole Ratio     |                       | 0.17                         | 0.10      | 0.13      | 0.08      | 0.19      | 0.02      | 0.432     | 0.268     | 0.400     | 0.43      | 0.273     | 0.222     |
| CM <sub>2</sub> to Feed Wt.       |                       | 0.1196                       | 0.1075    | 0.1014    | 0.0910    | 0.1368    | 0.065     | 0.237     | 0.116     | 0.173     | 0.152     | 0.111     | 0.0605    |
| Insolubles to CM <sub>2</sub> Wt. |                       | 0.027                        | -         | -         | 0.257     | 0.081     | 0.0189    | 0.007     | 0.045     | 0.022     | 0.0173    | 0.0122    | 0.0275    |
| Plant Productivity, lb/hr         |                       | 7                            | 9.7       | 3.7       | 9.9       | 8.9       | 5         | 21.4      | 10.5      | 15.5      | 13.7      | 10.0      | 5.45      |

## NOTES

Feeding to Reactors R204 → 7

Feeding Reactors R200 → 3 After Orifices in R200 → 7 Failed

TABLE II-1 (Continued)

| Date                             | 6/22  | 6/23  | 6/23  | 6/23  | 6/27  | 6/27  | 6/27  | 6/28   | 6/28  | 6/28  | 6/28  | 6/29  | 6/29   | 6/29   |
|----------------------------------|-------|-------|-------|-------|-------|-------|-------|--------|-------|-------|-------|-------|--------|--------|
| Sample No. Calculations Based On | 53    | 54    | 51    | 52    | 53    | 54    | 51    | 52     | 53    | 54    | 51    | 52    | 53     | 53     |
| Time                             | 11:15 | 14:30 | 01:30 | 05:30 | 08:30 | 14:00 | 08:00 | 02:00  | 07:00 | 11:00 | 14:00 | 02:00 | 06:00  | 10:00  |
| Reactor Steam Pressure, psig     | 225   | 225   | 225   | 225   | 195   | 195   | 200   | 190    | 195   | 190   | 194   | 190   | 190    | 190    |
| Effluent No. of Tubes            | 2-3   | 2-3   | 1     | 1     | 3     | 4     | 2     | W.R.   | 4     | 3     | 3     | 2.5   | 4      | 2-3    |
| 2 L. Feed Product                | 32.2  | 25.0  | 25.8  | 26.2  | 24.5  | 28.2  | 26.7  | 25.6   | 32.0  | 28.5  | 32.7  | 33.2  | 34.6   | 33.2   |
| 2 AS. Feed Product               | 26.6  | 18.9  | 18.9  | 22.6  | 18.9  | 22.6  | 19.6  | 12.6   | 15.4  | 16.6  | 15.7  | 20.7  | 21.6   | 25.2   |
| 2 DS. Feed Product               | 61.1  | 61.1  | 61.1  | 58.6  | 61.1  | 58.6  | 60.6  | 61.6   | 57.2  | 61.0  | 55.5  | 57.9  | 57.5   | 62.3   |
| 2 DS. Feed Product               | 61.1  | 61.1  | 61.1  | 58.6  | 61.1  | 58.6  | 60.6  | 61.6   | 57.2  | 61.0  | 55.5  | 57.9  | 57.5   | 62.3   |
| 2 Insulation, Product            | 13.7  | 13.7  | 13.7  | 13.7  | 13.7  | 13.7  | 13.7  | 13.7   | 13.7  | 13.7  | 13.7  | 13.7  | 13.7   | 13.7   |
| Feed Rate, lb/hr                 | 90    | 90    | 90    | 90    | 90    | 90    | 90    | 90     | 90    | 80    | 80    | 125   | 50     | 180    |
| Calculations                     |       |       |       |       |       |       |       |        |       |       |       |       |        |        |
| AS to W in React                 | 1.41  | 1.41  | 1.41  | 1.41  | 1.41  | 1.41  | 1.41  | 1.34   | N/A   | 1.61  | 1.27  | 1.31  | 1.24   | 1.41   |
| DS to W in React                 | 1.41  | 1.41  | 1.41  | 1.41  | 1.41  | 1.41  | 1.41  | 0.933  | -     | 0.457 | 0.195 | 0.306 | 0.338  | 0.293  |
| DS to W in React                 | 1.41  | 1.41  | 1.41  | 1.41  | 1.41  | 1.41  | 1.41  | 0.5665 | 0.234 | -     | 0.133 | 0.08  | 0.0875 | 0.0695 |
| Plant Production, lb/hr          | 1.41  | 1.41  | 1.41  | 1.41  | 1.41  | 1.41  | 1.41  | 0.42   | 0.024 | -     | 0.05  | 0.056 | 0.0478 | 0.0427 |
| Plant Production, lb/hr          | 1.41  | 1.41  | 1.41  | 1.41  | 1.41  | 1.41  | 1.41  | 1.10   | 21.1  | -     | 12.0  | 6.4   | 12.2   | 5.3    |

NOTES

Feed Rate Reactors 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45, 46, 47, 48, 49, 50, 51, 52, 53, 54, 55, 56, 57, 58, 59, 60, 61, 62, 63, 64, 65, 66, 67, 68, 69, 70, 71, 72, 73, 74, 75, 76, 77, 78, 79, 80, 81, 82, 83, 84, 85, 86, 87, 88, 89, 90, 91, 92, 93, 94, 95, 96, 97, 98, 99, 100, 101, 102, 103, 104, 105, 106, 107, 108, 109, 110, 111, 112, 113, 114, 115, 116, 117, 118, 119, 120, 121, 122, 123, 124, 125, 126, 127, 128, 129, 130, 131, 132, 133, 134, 135, 136, 137, 138, 139, 140, 141, 142, 143, 144, 145, 146, 147, 148, 149, 150, 151, 152, 153, 154, 155, 156, 157, 158, 159, 160, 161, 162, 163, 164, 165, 166, 167, 168, 169, 170, 171, 172, 173, 174, 175, 176, 177, 178, 179, 180, 181, 182, 183, 184, 185, 186, 187, 188, 189, 190, 191, 192, 193, 194, 195, 196, 197, 198, 199, 200, 201, 202, 203, 204, 205, 206, 207, 208, 209, 210, 211, 212, 213, 214, 215, 216, 217, 218, 219, 220, 221, 222, 223, 224, 225, 226, 227, 228, 229, 230, 231, 232, 233, 234, 235, 236, 237, 238, 239, 240, 241, 242, 243, 244, 245, 246, 247, 248, 249, 250, 251, 252, 253, 254, 255, 256, 257, 258, 259, 260, 261, 262, 263, 264, 265, 266, 267, 268, 269, 270, 271, 272, 273, 274, 275, 276, 277, 278, 279, 280, 281, 282, 283, 284, 285, 286, 287, 288, 289, 290, 291, 292, 293, 294, 295, 296, 297, 298, 299, 300, 301, 302, 303, 304, 305, 306, 307, 308, 309, 310, 311, 312, 313, 314, 315, 316, 317, 318, 319, 320, 321, 322, 323, 324, 325, 326, 327, 328, 329, 330, 331, 332, 333, 334, 335, 336, 337, 338, 339, 340, 341, 342, 343, 344, 345, 346, 347, 348, 349, 350, 351, 352, 353, 354, 355, 356, 357, 358, 359, 360, 361, 362, 363, 364, 365, 366, 367, 368, 369, 370, 371, 372, 373, 374, 375, 376, 377, 378, 379, 380, 381, 382, 383, 384, 385, 386, 387, 388, 389, 390, 391, 392, 393, 394, 395, 396, 397, 398, 399, 400, 401, 402, 403, 404, 405, 406, 407, 408, 409, 410, 411, 412, 413, 414, 415, 416, 417, 418, 419, 420, 421, 422, 423, 424, 425, 426, 427, 428, 429, 430, 431, 432, 433, 434, 435, 436, 437, 438, 439, 440, 441, 442, 443, 444, 445, 446, 447, 448, 449, 450, 451, 452, 453, 454, 455, 456, 457, 458, 459, 460, 461, 462, 463, 464, 465, 466, 467, 468, 469, 470, 471, 472, 473, 474, 475, 476, 477, 478, 479, 480, 481, 482, 483, 484, 485, 486, 487, 488, 489, 490, 491, 492, 493, 494, 495, 496, 497, 498, 499, 500, 501, 502, 503, 504, 505, 506, 507, 508, 509, 510, 511, 512, 513, 514, 515, 516, 517, 518, 519, 520, 521, 522, 523, 524, 525, 526, 527, 528, 529, 530, 531, 532, 533, 534, 535, 536, 537, 538, 539, 540, 541, 542, 543, 544, 545, 546, 547, 548, 549, 550, 551, 552, 553, 554, 555, 556, 557, 558, 559, 560, 561, 562, 563, 564, 565, 566, 567, 568, 569, 570, 571, 572, 573, 574, 575, 576, 577, 578, 579, 580, 581, 582, 583, 584, 585, 586, 587, 588, 589, 590, 591, 592, 593, 594, 595, 596, 597, 598, 599, 600, 601, 602, 603, 604, 605, 606, 607, 608, 609, 610, 611, 612, 613, 614, 615, 616, 617, 618, 619, 620, 621, 622, 623, 624, 625, 626, 627, 628, 629, 630, 631, 632, 633, 634, 635, 636, 637, 638, 639, 640, 641, 642, 643, 644, 645, 646, 647, 648, 649, 650, 651, 652, 653, 654, 655, 656, 657, 658, 659, 660, 661, 662, 663, 664, 665, 666, 667, 668, 669, 670, 671, 672, 673, 674, 675, 676, 677, 678, 679, 680, 681, 682, 683, 684, 685, 686, 687, 688, 689, 690, 691, 692, 693, 694, 695, 696, 697, 698, 699, 700, 701, 702, 703, 704, 705, 706, 707, 708, 709, 710, 711, 712, 713, 714, 715, 716, 717, 718, 719, 720, 721, 722, 723, 724, 725, 726, 727, 728, 729, 730, 731, 732, 733, 734, 735, 736, 737, 738, 739, 740, 741, 742, 743, 744, 745, 746, 747, 748, 749, 750, 751, 752, 753, 754, 755, 756, 757, 758, 759, 760, 761, 762, 763, 764, 765, 766, 767, 768, 769, 770, 771, 772, 773, 774, 775, 776, 777, 778, 779, 780, 781, 782, 783, 784, 785, 786, 787, 788, 789, 790, 791, 792, 793, 794, 795, 796, 797, 798, 799, 800, 801, 802, 803, 804, 805, 806, 807, 808, 809, 810, 811, 812, 813, 814, 815, 816, 817, 818, 819, 820, 821, 822, 823, 824, 825, 826, 827, 828, 829, 830, 831, 832, 833, 834, 835, 836, 837, 838, 839, 840, 841, 842, 843, 844, 845, 846, 847, 848, 849, 850, 851, 852, 853, 854, 855, 856, 857, 858, 859, 860, 861, 862, 863, 864, 865, 866, 867, 868, 869, 870, 871, 872, 873, 874, 875, 876, 877, 878, 879, 880, 881, 882, 883, 884, 885, 886, 887, 888, 889, 890, 891, 892, 893, 894, 895, 896, 897, 898, 899, 900, 901, 902, 903, 904, 905, 906, 907, 908, 909, 910, 911, 912, 913, 914, 915, 916, 917, 918, 919, 920, 921, 922, 923, 924, 925, 926, 927, 928, 929, 930, 931, 932, 933, 934, 935, 936, 937, 938, 939, 940, 941, 942, 943, 944, 945, 946, 947, 948, 949, 950, 951, 952, 953, 954, 955, 956, 957, 958, 959, 960, 961, 962, 963, 964, 965, 966, 967, 968, 969, 970, 971, 972, 973, 974, 975, 976, 977, 978, 979, 980, 981, 982, 983, 984, 985, 986, 987, 988, 989, 990, 991, 992, 993, 994, 995, 996, 997, 998, 999, 1000.



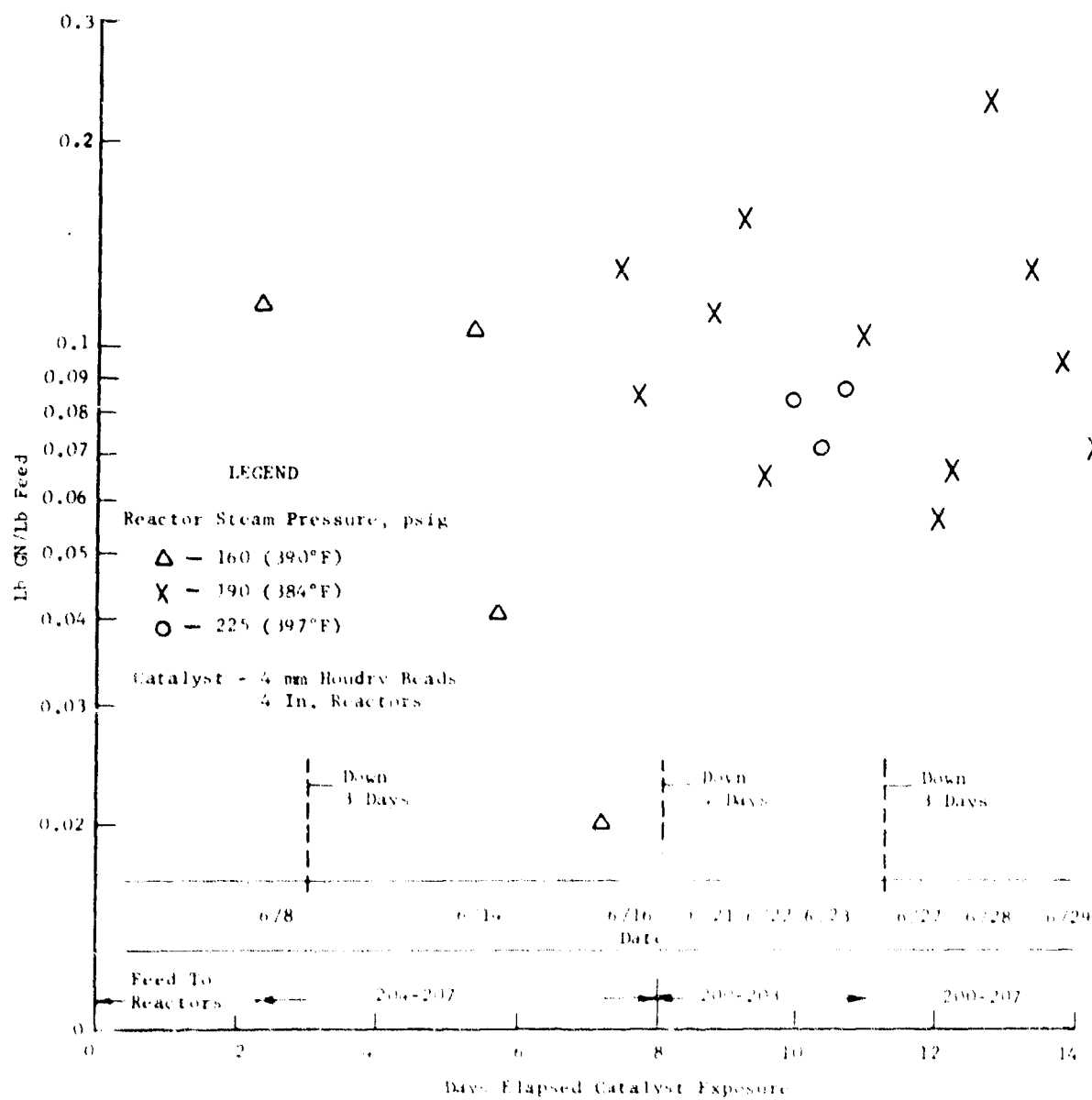


Figure II-12. Productivity Vs Time - First Catalyst Run

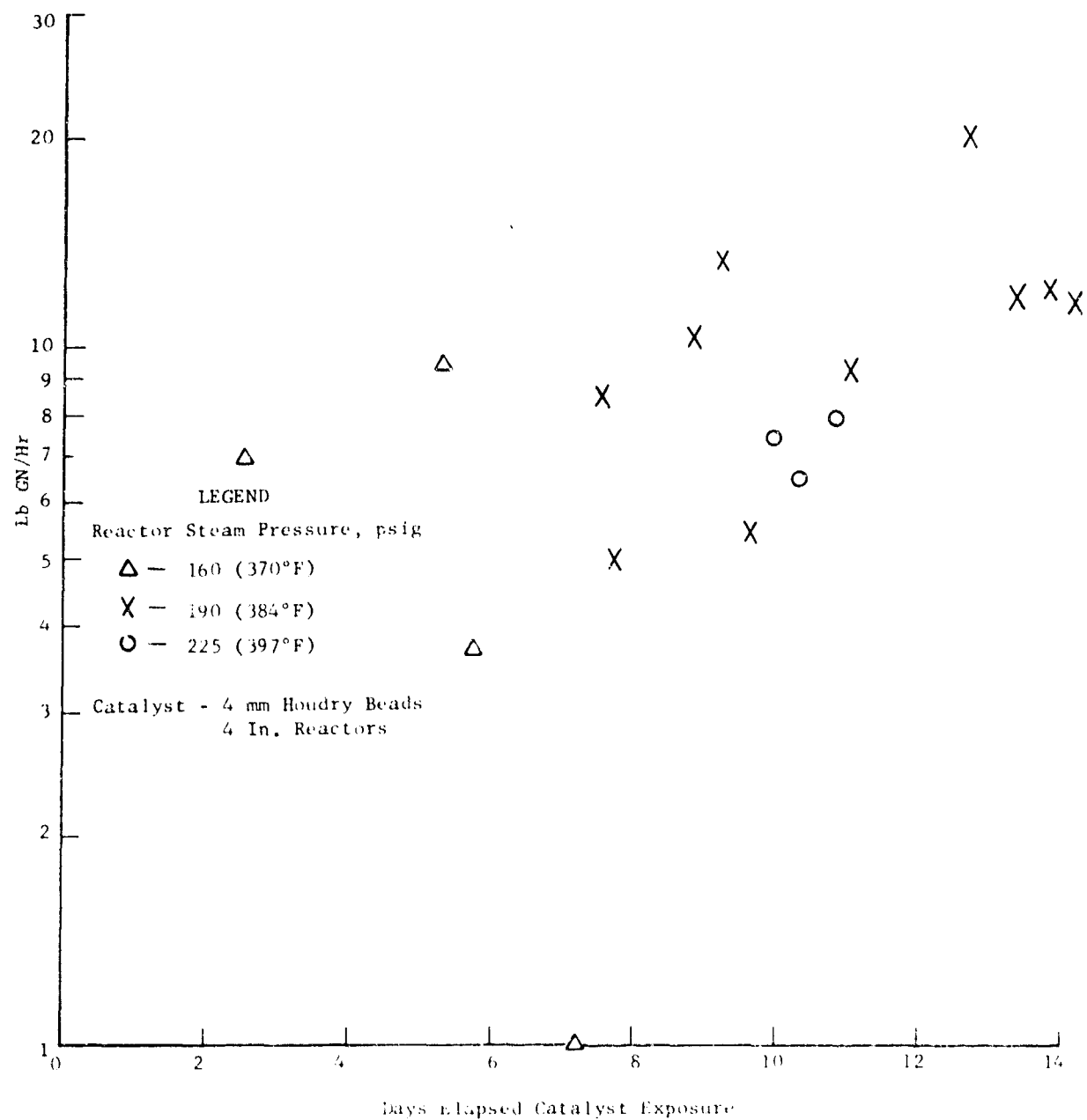


Figure II-13. Productivity/Hr Vs. Time - First Catalyst Run

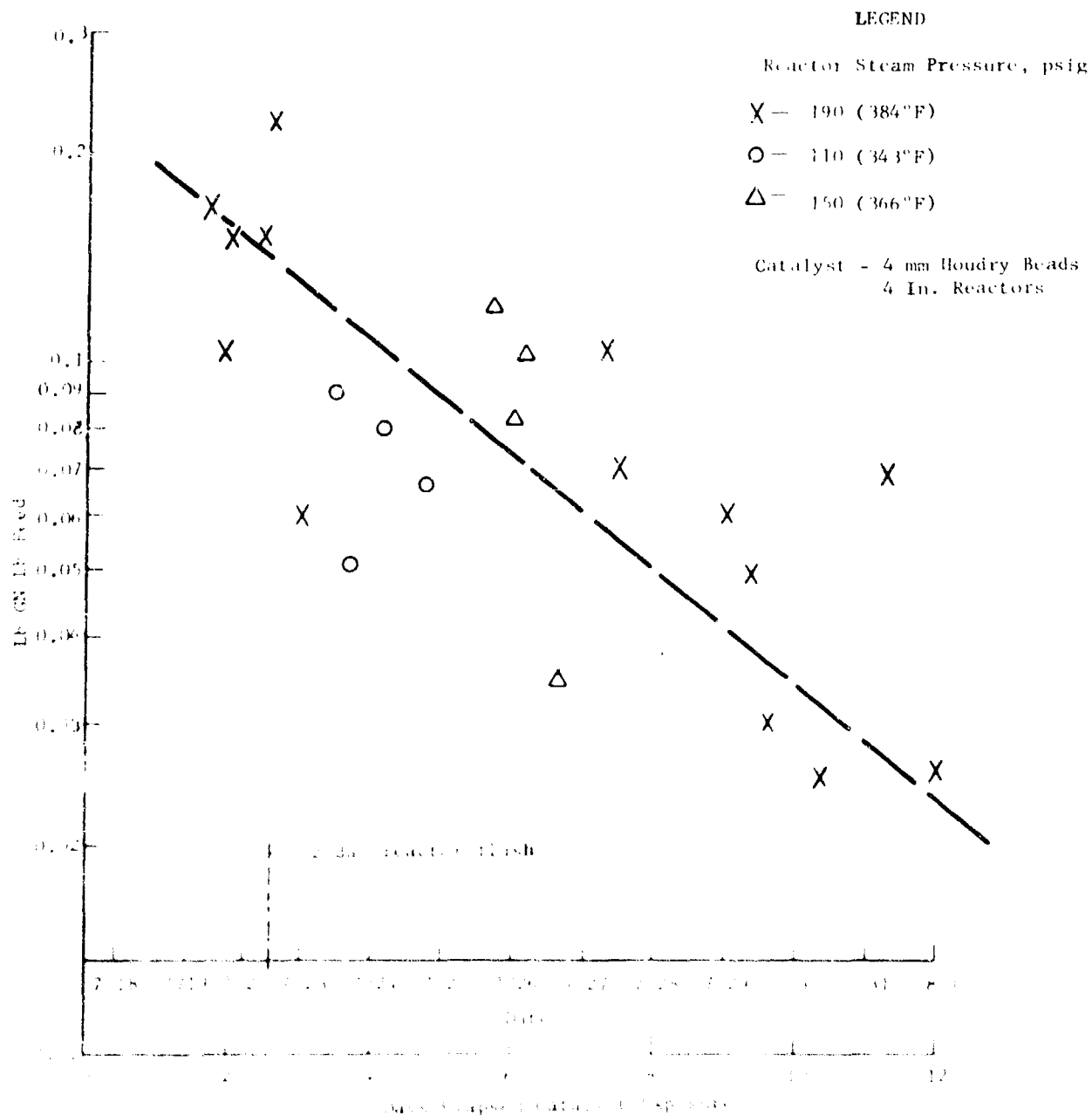


Figure 11-14. Productivity Vs. Time - Second Catalyst Run

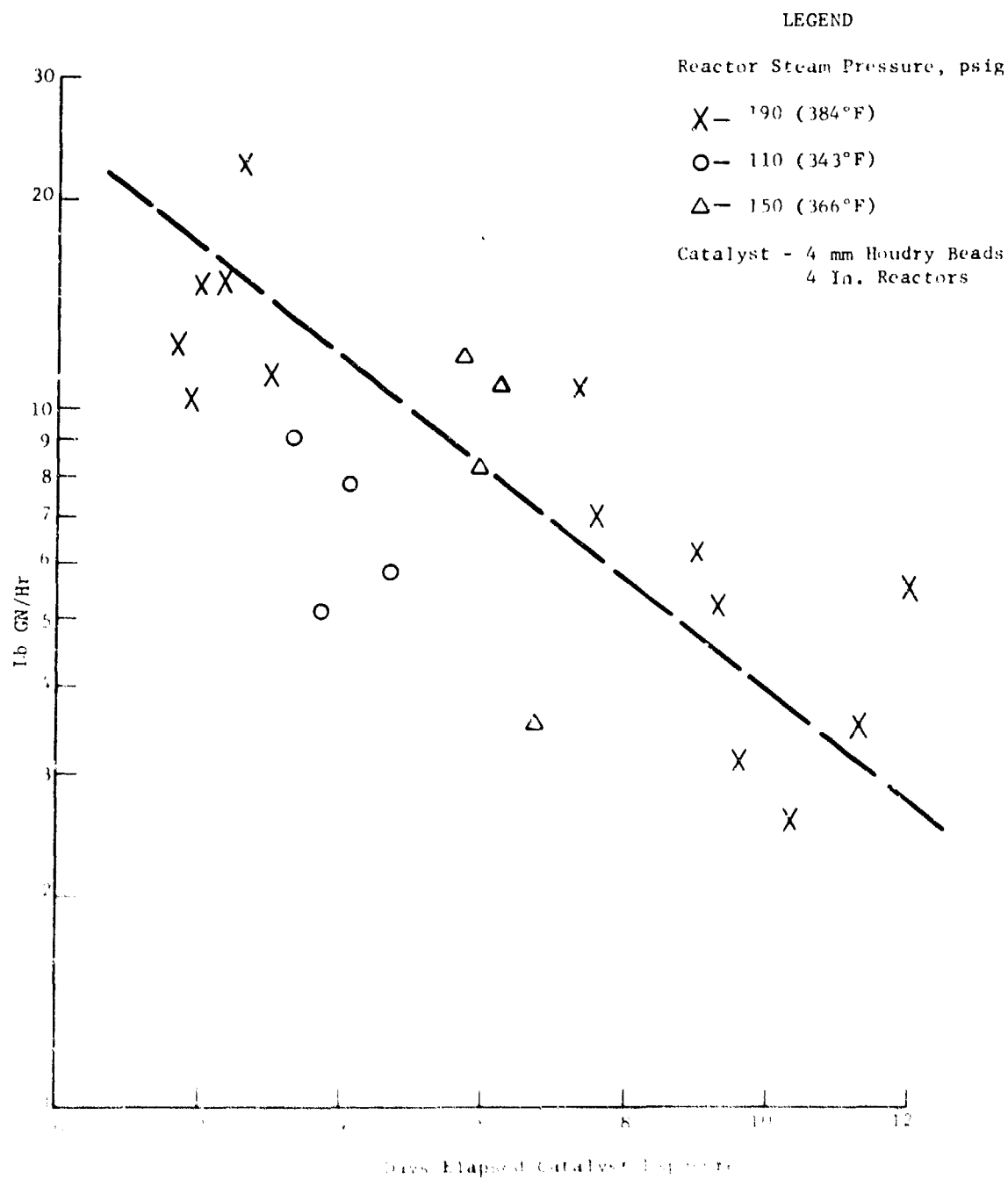


Figure II-15. Productivity/Hr Vs Time - Second Catalyst Run

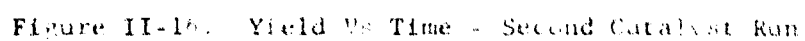


TABLE II-2

**REACTOR PERFORMANCE**  
(Operating Conditions and Calculated Results)

Run No. 2 (7/19/72 → 8/1/72)

| Date                               | 7/21 |      |      |      |      |      |      |      |      |      | 7/24 - 2000 - Raised steam pressure to 150 psia (185°C) |        |        |       |       |        |        |        |        |       |
|------------------------------------|------|------|------|------|------|------|------|------|------|------|---|--------|--------|-------|-------|--------|--------|--------|--------|-------|
|                                    | 7/21 | 7/21 | 7/21 | 7/21 | 7/21 | 7/21 | 7/21 | 7/21 | 7/21 | 7/21 | 7/23  | 7/23   | 7/23   | 7/23  | 7/23  | 7/23   | 7/23   | 7/23   | 7/23   | 7/23  |
| Sample No. - Calculations Based On | S1   | S2   | S3   | S1   | S1   | S1   | S1   | S1   | S1   | S1   | S1  | S3     | S5     | S1    | S2    | S3     | S1     | S2     | S3     | S1    |
| Time                               | 1:30 | 1:45 | 2:00 | 2:15 | 2:30 | 2:45 | 3:00 | 3:15 | 3:30 | 3:45 | 15:30   | 15:30  | 23:30  | 04:30 | 08:30 | 13:00  | 04:30  | 08:30  | 13:00  | 09:30 |
| <b>Data</b>                        |      |      |      |      |      |      |      |      |      |      |   |        |        |       |       |        |        |        |        |       |
| Reactor Steam Pressure, psia       | 160  | 145  | 140  | 140  | 140  | 140  | 140  | 140  | 140  | 140  | 110   | 110    | 115    | 110   | 100   | 110    | 110    | 100    | 110    | 150   |
| Exhaustive No. of Tubes            | 8    | 8    | 8    | 8    | 8    | 8    | 8    | 8    | 8    | 8    | 8   | 8      | 8      | 8     | 8     | 8      | 8      | 8      | 8      | 8     |
| Feed Product                       | 13.7 | 13.7 | 13.7 | 13.7 | 13.7 | 13.7 | 13.7 | 13.7 | 13.7 | 13.7 | 33.7  | 34.9   | 33.3   | -     | -     | 27.4   | 27.4   | 27.4   | 27.4   | -     |
| Feed Product                       | 13.7 | 13.7 | 13.7 | 13.7 | 13.7 | 13.7 | 13.7 | 13.7 | 13.7 | 13.7 | 19.5  | 19.6   | 23.4   | 32.7  | 27.2  | 24.6   | 24.6   | 24.6   | 24.6   | -     |
| Feed Product                       | 13.7 | 13.7 | 13.7 | 13.7 | 13.7 | 13.7 | 13.7 | 13.7 | 13.7 | 13.7 | 58.4  | 56.8   | 59.0   | -     | -     | 60.4   | 60.4   | 60.4   | 60.4   | -     |
| Feed Product                       | 13.7 | 13.7 | 13.7 | 13.7 | 13.7 | 13.7 | 13.7 | 13.7 | 13.7 | 13.7 | 63.7  | 63.3   | 60.5   | 61.2  | 61.0  | 61.6   | 61.6   | 61.6   | 61.6   | -     |
| Feed Product                       | 13.7 | 13.7 | 13.7 | 13.7 | 13.7 | 13.7 | 13.7 | 13.7 | 13.7 | 13.7 | 3.0   | 6.1    | 4.1    | -     | -     | 6.2    | 6.2    | 6.2    | 6.2    | -     |
| Feed Product                       | 13.7 | 13.7 | 13.7 | 13.7 | 13.7 | 13.7 | 13.7 | 13.7 | 13.7 | 13.7 | 14.6  | 15.2   | 13.4   | 3.2   | 8.5   | 13.0   | 13.0   | 13.0   | 13.0   | -     |
| Feed Product                       | 13.7 | 13.7 | 13.7 | 13.7 | 13.7 | 13.7 | 13.7 | 13.7 | 13.7 | 13.7 | 0.98  | 0.30   | 0.10   | -     | Trace | 0.04   | 0.04   | 0.04   | 0.04   | -     |
| Feed Rate, lb/hr                   | 30   | 30   | 30   | 30   | 30   | 30   | 30   | 30   | 30   | 30   | 100   | 100    | 100    | 100   | 100   | 100    | 100    | 100    | 100    | 100   |
| <b>Calculated Data</b>             |      |      |      |      |      |      |      |      |      |      |   |        |        |       |       |        |        |        |        |       |
| AS - Feed Rate                     | 170  | 170  | 170  | 170  | 170  | 170  | 170  | 170  | 170  | 170  | 1.30  | 1.13   | 1.32   | -     | -     | 1.65   | 1.65   | 1.65   | 1.65   | 1.84  |
| AS - Feed Rate                     | 170  | 170  | 170  | 170  | 170  | 170  | 170  | 170  | 170  | 170  | 0.251   | 0.121  | 0.311  | -     | -     | 0.598  | 0.598  | 0.598  | 0.598  | -     |
| AS - Feed Rate                     | 170  | 170  | 170  | 170  | 170  | 170  | 170  | 170  | 170  | 170  | 0.909   | 0.0513 | 0.0788 | -     | -     | 0.0575 | 0.0575 | 0.0575 | 0.0575 | -     |
| AS - Feed Rate                     | 170  | 170  | 170  | 170  | 170  | 170  | 170  | 170  | 170  | 170  | 0.0073  | 0.044  | 0.011  | -     | -     | 0.006  | 0.006  | 0.006  | 0.006  | -     |
| AS - Feed Rate                     | 170  | 170  | 170  | 170  | 170  | 170  | 170  | 170  | 170  | 170  | 9.0   | 5.1    | 7.9    | -     | -     | 5.8    | 5.8    | 5.8    | 5.8    | -     |

NOTES:

Start July 17, New Catalysts: First Data 7/19, Flow to All Reactors

| Date                                  | 7/25 | 7/25 | 7/25 | 7/26 | 7/26 | 7/26 | 7/26 | 7/27 | 7/27  | 7/27  | 7/27 | 7/27 | 7/28 |
|---------------------------------------|------|------|------|------|------|------|------|------|-------|-------|------|------|------|
| Sample No.                            | 52   | S1   | S4   | S1   | S2   | S3   | S4   | S1   | S2    | S3    | S4   | S5   | -    |
| Time                                  | 1400 | 1730 | 1730 | 0330 | 0530 | 0330 | 1200 | 0130 | 0430  | 0830  | 1230 | 2000 | 1030 |
| Reactor Steam Pressure, psig          | 150  | 150  | 150  | 150  | 150  | 150  | 155  | 185  | 185   | 185   | 185  | 195  |      |
| Effective No. of Tubes                | 8    | 8    | 8    | -    | -    | -    | -    | 8    | 8     | 8     | 8    | 8    |      |
| % Aq. Feed/Product                    | 28.6 | 28.6 | 29.9 | 29.4 | 30.4 | -    | 28.5 | -    | 31.4  | 31.4  | -    | -    |      |
| % Aq. Feed/Product                    | 41.3 | 41.3 | 42.1 | 41.7 | 42.2 | -    | 41.5 | -    | 41.7  | 41.7  | -    | -    |      |
| % Aq. Feed/Product                    | 59.7 | 59.7 | 60.8 | 59.7 | 60.7 | -    | 60.9 | -    | 60.0  | 60.0  | -    | -    |      |
| % Insulation Product                  | 7.2  | 7.2  | 7.2  | 7.2  | 7.2  | -    | 7.2  | -    | 7.2   | 7.2   | -    | -    |      |
| % Insulation Product                  | 17.1 | 17.1 | 17.1 | 17.1 | 17.1 | -    | 17.1 | -    | 17.1  | 17.1  | -    | -    |      |
| % Insulation Product                  | 9.2  | 9.2  | 9.2  | 9.2  | 9.2  | -    | 9.2  | -    | 9.2   | 9.2   | -    | -    |      |
| Feed Rate, lb/hr                      | 100  | 100  | 100  | 100  | 100  | 100  | 100  | 100  | 100   | 100   | 100  | 100  |      |
| Calculated                            |      |      |      |      |      |      |      |      |       |       |      |      |      |
| AN to H <sub>2</sub> O Ratio          | 1.34 | 1.34 | 1.34 | 1.37 | 1.34 | -    | 1.49 | -    | 1.40  | 1.40  | -    | -    |      |
| AN to H <sub>2</sub> O (2.00 to 4.00) | 1.34 | 1.34 | 1.34 | 1.34 | 1.34 | -    | 1.34 | -    | 1.357 | 1.357 | -    | -    |      |
| AN to Feed Wt.                        | 1.23 | 1.23 | 1.23 | 1.24 | 1.24 | -    | 1.35 | -    | 1.11  | 1.11  | -    | -    |      |
| Insulation, GSC Wt.                   | 1.33 | 1.33 | 1.33 | 1.33 | 1.33 | -    | 1.33 | -    | 1.33  | 1.33  | -    | -    |      |
| Plant Productivity, lb/hr             | 10.3 | 10.3 | 10.3 | 10.3 | 10.3 | -    | 10.3 | -    | 10.3  | 10.3  | -    | -    |      |

TABLE II-2 (Continued)

| Date                             | 7/28 | 7/28 | 7/28  | 7/29  | 7/29  | 7/29 | 7/30 | 7/30   | 7/30 | 7/30  | 7/31 | 7/31 | 7/31  | 7/31 | 8/1  |
|----------------------------------|------|------|-------|-------|-------|------|------|--------|------|-------|------|------|-------|------|------|
| Sample No. Calculations Based on | S1   | S2   | S3    | S1    | S2    | S3   |      |        |      |       |      |      |       |      |      |
| Time                             | 0430 | 1130 | 2000  | 0400  | 1200  | 2000 | 0430 | 1200   | 2130 | 0430  | 1200 | 1630 | 2030  | 2030 | 1500 |
| Reactor Steam Pressure, psia     | 17   | 160  | 197   | 190   | 190   | 190  | 198  | 190    | 190  | 190   | 195  | 195  | 190   | 190  |      |
| Effective No. of Tubes           | 8    | 8    | 8     | 8     | 8     | 8    | 8    | 8      | 8    | 8     | 8    | 8    | 8     | 8    |      |
| W. Feed Product                  | -    | -    | 30.9/ | 31.4/ | 29.5/ | -    | -    | 28.9/  | -    | 22.8/ | -    | -    | 28.4/ | -    |      |
|                                  |      |      | 19.3  | 20.8  | 22.1  |      |      | 23.6   |      | 17.4  |      |      | 23.1  |      |      |
| 2 AN, Feed Product               | -    | -    | 57.1/ | 56.1/ | 58.9/ | -    | -    | 59.4/  | -    | 62.0/ | -    | -    | 58.5/ | -    |      |
|                                  |      |      | 43.4  | 40    | 58.1  |      |      | 58.6   |      | 60.3  |      |      | 60.6  |      |      |
| 2 ON, Feed Product               | -    | -    | 4.6/  | 8.8/  | 11.0/ | -    | -    | 8.8/   | -    | 9.7/  | -    | -    | 4.0/  | -    |      |
|                                  |      |      | 15.1  | 15.7  | 15.4  |      |      | 17.5   |      | 17.6  |      |      | 7.9   |      |      |
| 2 Insoluble, Product             | -    | -    | 0.60  | 0.53  | 0.65  | -    | -    | 0.50   | -    | 0.2   | -    | -    | -     | -    |      |
| Feed Rate, lb/hr                 | 100  | 105  | 107   | 105   | 105   | 127  | 125  | 125    | 50   | 50    | 50   | 180  | 180   | 180  |      |
| Calculations                     |      |      |       |       |       |      |      |        |      |       |      |      |       |      |      |
| AN, lb/hr Ratio                  | -    | -    | 1.14  | 1.34  | 1.49  | -    | -    | 1.54   | -    | 2.04  | -    | -    | 1.51  | -    |      |
| 2 ON No. (2 ON No. M. I. Basis)  | -    | -    | 0.027 | 0.19  | 0.192 | -    | -    | 0.222  | -    | 0.553 | -    | -    | 0.210 | -    |      |
| 2 ON, Feed, wt.                  | -    | -    | 0.04  | 0.05  | 0.05  | -    | -    | 0.026  | -    | 0.07  | -    | -    | 0.026 | -    |      |
| 2 Insoluble, Feed, wt.           | -    | -    | 0.002 | 0.004 | 0.005 | -    | -    | 0.0192 | -    | 0.026 | -    | -    | -     | -    |      |
| Plant Productivity, lb/hr        | -    | -    | 4.36  | 5.13  | 3.42  | -    | -    | 2.62   | -    | 3.45  | -    | -    | 5.6   | -    |      |

NOTES:

Boiler  
Problems



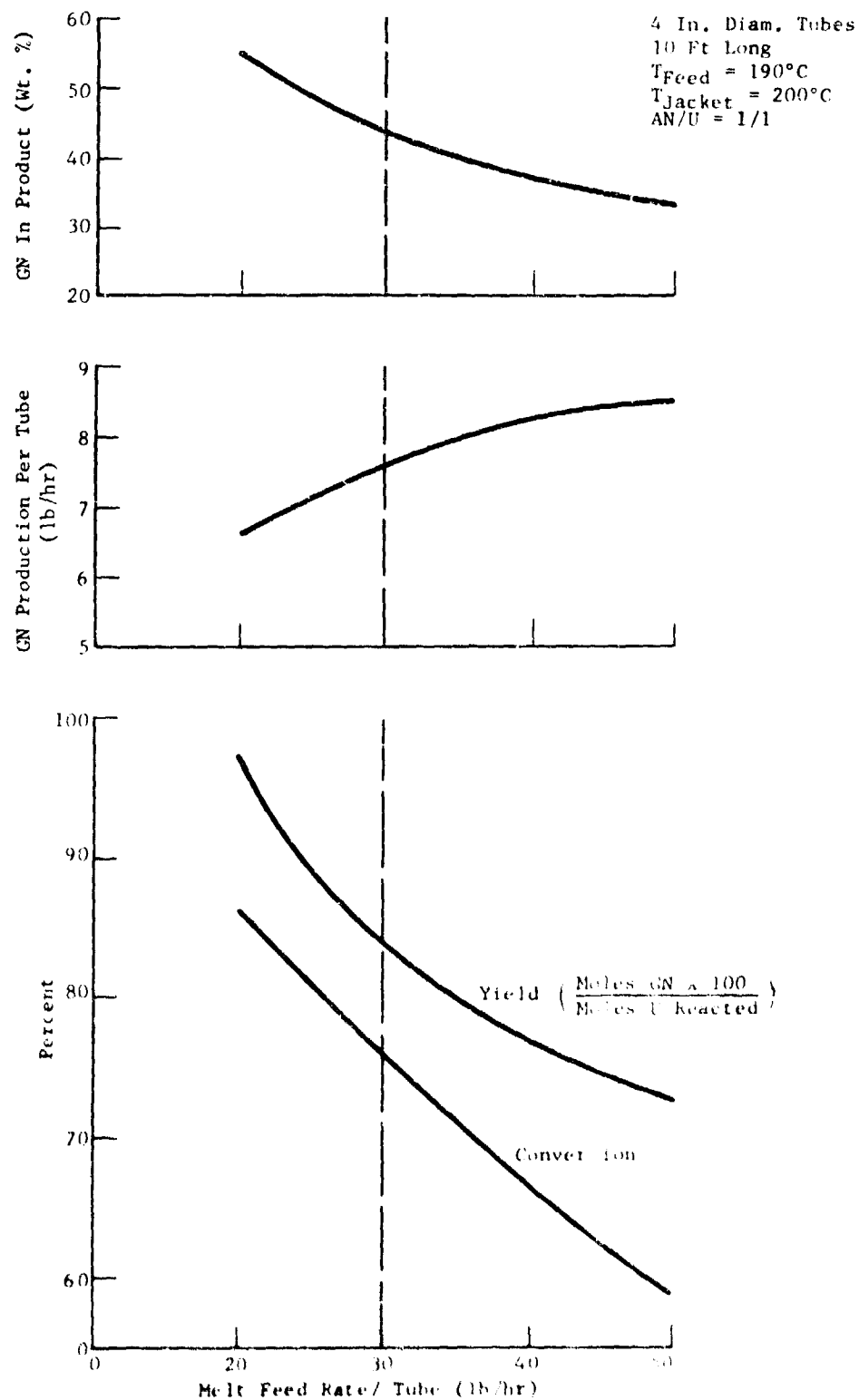


Figure II-17. Computer Prediction

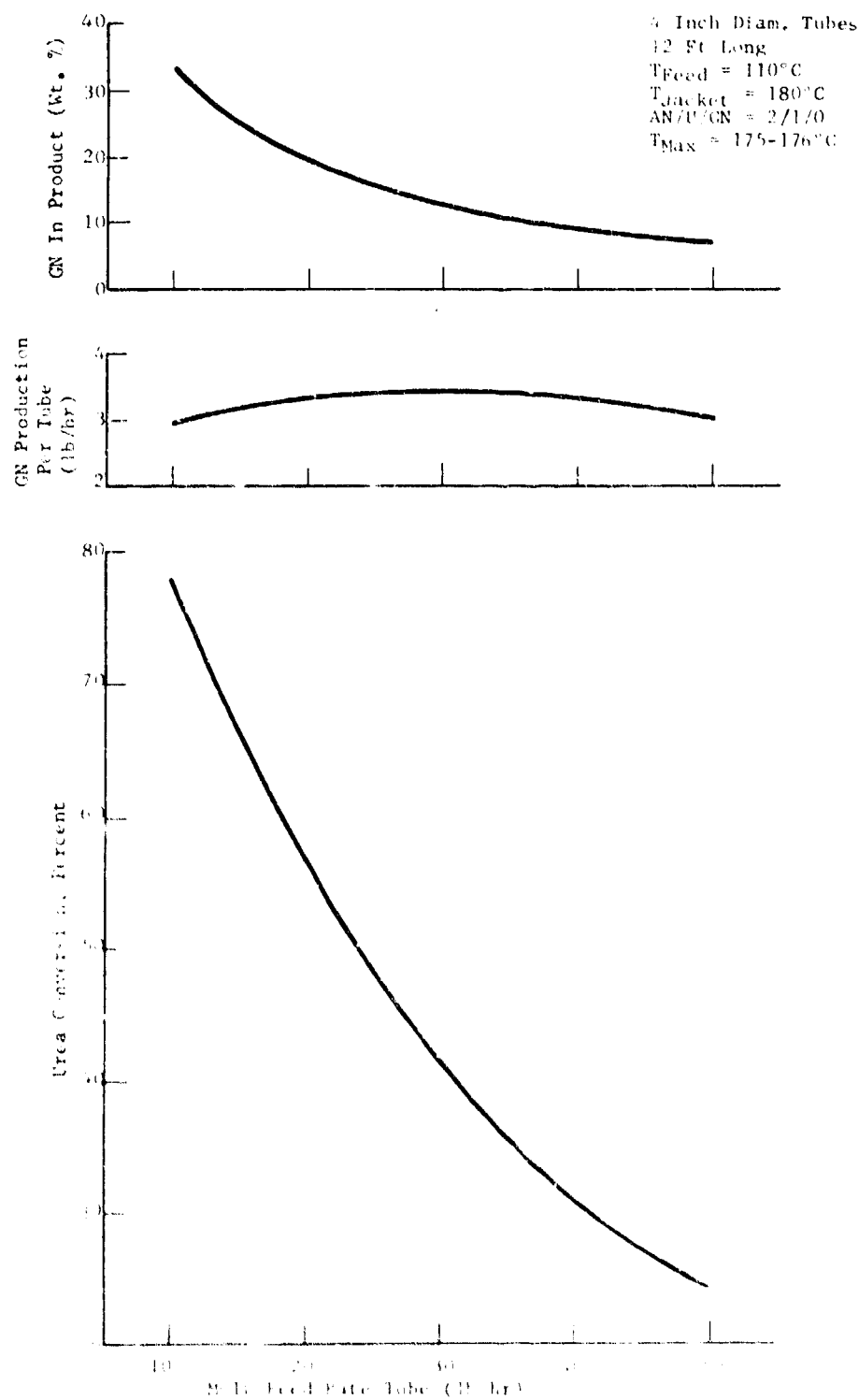
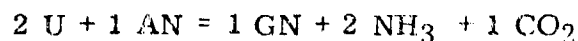


Figure II-18. Computer Prediction

TABLE II-3

## SAMPLE CALCULATIONS FOR DETERMINING REACTOR YIELD AND PRODUCTIVITY

I Step by StepBasis: Moles Nitrate are consumed.

(For every mole of AN consumed, one mole of guanidine nitrate is formed.)

Data: Reactor Steam Pressure = 225 psig

Feed Rate = 90 lb/hr

Analyses

|                   | Feed |        |         | Product |        |         |
|-------------------|------|--------|---------|---------|--------|---------|
|                   | %    | Lbs. * | Moles** | %       | Lbs. * | Moles** |
| Urea              | 25.8 | 25.8   | .430    | 16.9    | 16.9   | .282    |
| Ammonium Nitrate  | 63.3 | 63.3   | .791    | 62.4    | 62.4   | .780    |
| Guanidine Nitrate | 7.4  | 7.4    | .0606   | 18.4    | 18.4   | .151    |
| Insolubles        | -    | -      | -       | 0.38    | 0.38   | .003    |

\* - Arbitrarily based on 100 lbs. of total material

\*\* - Calculated moles based on arbitrary 100 lbs. material

$$\text{Total Moles of Nitrate in Feed/100 lbs. Feed} = \text{Moles AN} + \text{Moles GN} \\ = 0.8516$$

$$\text{Total Moles of Nitrate in Product/100 lbs. Product} = 0.931$$

$$\frac{\text{Moles of Urea in Feed}}{100 \text{ lbs. Feed}} \div \frac{\text{Moles of Nitrate in Feed}}{100 \text{ lbs. Feed}} = \left( \frac{\text{Moles Urea}}{\text{Moles Nitrate}} \right)_{\text{Feed}} = \left( \frac{\text{U}_M}{\text{N}} \right)_F = \frac{.430}{.8516} = .505$$

$$\frac{\text{Moles Urea in Product}}{100 \text{ lbs. Product}} \div \frac{\text{Moles of Total Nitrates in Product}}{100 \text{ lbs. Product}} = \left( \frac{\text{Moles Urea}}{\text{Moles Nitrate}} \right)_{\text{Product}} = \left( \frac{\text{U}_M}{\text{N}} \right)_P = \frac{.282}{.931} = .303$$

TABLE II-3 (Continued)

Similarly:

$$\left(\frac{GN_M}{N}\right)_{\text{feed}} = \frac{.0606}{.8516} = 0.0712 \quad \left(\frac{GN_M}{N}\right)_{\text{Product}} = \frac{.151}{.931} = 0.162$$

$$\left(\frac{AM}{N}\right)_{\text{feed}} = 0 \quad \left(\frac{AM}{N}\right)_{\text{Product}} = \frac{.003}{.931} = 0.0032$$

During the Reaction, then -

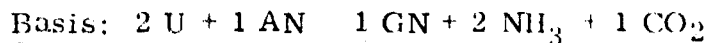
$$\Delta \left(\frac{U_M}{N}\right) = \left(\frac{U_M}{N}\right)_{\text{Feed}} - \left(\frac{U_M}{N}\right)_{\text{Product}} = 0.505 - 0.303 = 0.202$$

$$\Delta \left(\frac{GN_M}{N}\right) = \left(\frac{GN_M}{N}\right)_{\text{Feed}} - \left(\frac{GN_M}{N}\right)_{\text{Product}} = 0.0712 - 0.162 = -0.091$$

Or a loss of 0.202 moles urea per nitrate mole and a gain of 0.091 moles GN per nitrate mole.

$$\text{Feed Mole Ratio} \quad \left(\frac{AN_M}{U_M}\right)_{\text{Feed}} = 0.791/0.430 = 1.84$$

Yield



or 2 moles U consumed per mole of GN made.

$$\begin{aligned} \text{Yield} &= \frac{\text{Moles GN made}}{\text{Moles U consumed}/2} \times 100 \\ &= \frac{GN_M}{U_M} \times 200 - \frac{\left(\frac{GN_M}{N}\right)}{\left(\frac{U_M}{N}\right)} \times 200 \end{aligned}$$

$$\text{Yield} = \frac{0.091}{0.202} \times 200 = 89.9\%$$

Productivity

Productivity/lb. Feed = lbs. GN Made/lb. Feed

$$= \left(\frac{\text{Moles GN Made}}{\text{Moles Total Nitrate}}\right) \times \frac{\text{Moles Nitrate in Feed} \times \text{M. W. GN}}{100 \text{ lbs. Feed}}$$

TABLE II-3 (Continued)

$$\text{Productivity/lb. Feed} = \frac{\Delta \text{GN}_M}{N} \times \frac{N_{\text{Feed}}}{100} \times 122 =$$

$$0.091 \times 0.8516 \times 1.22$$

$$\underline{\text{Productivity/lb. Feed} = \text{Lbs. GN Made/lb. Feed} = 0.0945}$$

### Plant Productivity

$$\text{Plant Productivity} = \text{Lbs. GN Made/Hour}$$

$$= \frac{\text{Lbs. GN Made} \times \text{Lbs. Feed / Hr.}}{\text{lb. Feed}}$$

$$= 0.0945 \times 90 \text{ lbs. /hr.}$$

$$\underline{\text{Plant Productivity} = 8.5 \text{ lbs. /hr.}}$$

### Insolubles Formation

$$\text{Insolubles Productivity} = \frac{\Delta \text{AM}}{N} \times \frac{N_{\text{Feed}}}{100 \text{ lbs. Feed}} \times \text{M. W.} \times \text{Feed Rate}$$

$$= 0.0032 \times 0.8516 \times 1.28 \times 90 \text{ lb/hr}$$

$$= 0.314 \text{ lbs/hr.}$$

$$\text{Productivity Insolubles/Guanidine Nitrate} = 0.314/8.5 = 0.037$$

TABLE II-3 (Continued)

II. Alternative Calculation ProcedureNomenclature

|          |                 |    |                   |            |
|----------|-----------------|----|-------------------|------------|
| $X_j$    | total weight    |    |                   |            |
| $x_{ij}$ | weight fraction |    |                   |            |
| $y_{ij}$ | moles           |    |                   |            |
| $i$      | 1 = feed        |    | 2 = liquid output |            |
| $j$      | 1               | 2  | 3                 | 4          |
| Compound | GN              | AN | U                 | INSOLUBLES |
| Mw       | 122             | 80 | 60                | UNKNOWN    |

$$1. \quad y_{ij} = X_j x_{ij} / M_{w_j}$$

$$2. \quad y_{11} + y_{12} = \left[ \frac{x_{11}}{M_{w_1}} + \frac{x_{12}}{M_{w_2}} \right] X_1 = \left[ \frac{x_{21}}{M_{w_1}} + \frac{x_{22}}{M_{w_2}} \right] X_2 = y_{21} + y_{22}$$

$$3. \quad X_1 = \beta X_2$$

$$\text{Where: } \beta = \frac{x_{11} + x_{12} M_{w_1} / M_{w_2}}{x_{21} + x_{22} M_{w_1} / M_{w_2}} = \frac{x_{11} + 1.525 x_{12}}{x_{21} + 1.525 x_{22}}$$

$$\text{Yield} = \frac{-200 (x_{11} - x_{21} \beta) / M_{w_1}}{(x_{13} - x_{23} \beta) / M_{w_3}} = \frac{-98.36 (x_{11} - x_{21} \beta)}{x_{13} - x_{23} \beta}$$

$$\text{GN Productivity Rate} = (x_{11} - x_{21} \beta) \dot{X}_1$$

$$\text{INSOLUBLE FORMATION RATE} = x_{24} \beta \dot{X}_1 \quad (x_{14} = 0)$$

$$\text{INSOLUBLE PRODUCT RATIO} = - \frac{x_{24}}{x_{11} / \beta + x_{21}} \quad (x_{14} = 0)$$

TABLE II-3 (Continued)

Sample Calculations (using data from prior method)

$$1. \quad \beta = \frac{x_{11} + 1.525 x_{12}}{x_{21} + 1.525 x_{22}} = \frac{.074 + 1.525(.633)}{.184 + 1.525(.624)} = .9152$$

$$2. \quad Y = \frac{-98.36 (x_{11} - x_{21} \beta)}{x_{13} - x_{23} \beta} = \frac{-98.36 (.074 - .184 (.9152))}{.258 - .169 (.9152)} = 89.9\%$$

$$3. \quad \text{GN PRODUCTIVITY RATE} = (x_{11} - x_{21} \beta) \dot{X}_1$$

From (2),  $(x_{11} - x_{21} \beta) = .0944$

$\therefore \text{GN} = .0944 (90) = 8.5 \text{ LBS/HR}$

$$4. \quad \text{INSOLUBLE FORMATION RATE} = x_{24} \beta \dot{X}_1 = .0038 (.9152) (90) = .313 \frac{\text{LBS}}{\text{HR}}$$

$$5. \quad \text{RATIO} = -\frac{x_{24}}{x_{11}/\beta + x_{21}} = \frac{-.0038}{.074/.9152 - .184} = .0369$$

APPENDIX III

PHASE III, PART 2

RESOLUTION OF CATALYST POISONING PROBLEM



TABLE III-1

[illegible]

TABLE III-2

## DETAILED DATA FOR GRACE 59 SILICA GEL

| Call No.  | Run No. | 200°C Wt. Loss |     |     | Sample Temp. (°C) | Sample Time (hr) | Analytical Results |     |     | Residuals |     |     | Final Reactor Melt (g) | Moles of |        | Yield (%) | U Comp. | Moles of |        | Moles of | Moles of |
|---|---------|----------------|-----|-----|-------------------|------------------|--------------------|-----|-----|-----------|-----|-----|------------------------|----------|--------|-----------|---------|----------|--------|----------|----------|
|   |         | AF             | 1   | 2   |                   |                  | AF                 | 1   | 2   | AF        | 1   | 2   |                        | Reacted  | Formed |           |         | Reacted  | Formed |          |          |
| Grace Grade 59<br>Silica Gel  | 52-6    | NC             | 180 | 150 | 170               | 180              | 180                | 180 | 180 | 180       | 180 | 180 | 180                    | 1.480    | 0.4514 | 61.0      | 49.3    | 1.480    | 0.4514 | 61.0     | 49.3     |
|   | 52-7    | NC             | 180 | 150 | 170               | 180              | 180                | 180 | 180 | 180       | 180 | 180 | 180                    | 1.953    | 0.5095 | 72.7      | 65.1    | 1.953    | 0.5095 | 72.7     | 65.1     |
|   | 52-8    | NC             | 180 | 150 | 170               | 180              | 180                | 180 | 180 | 180       | 180 | 180 | 180                    | 2.792    | 1.254  | 82.1      | 63.2    | 2.792    | 1.254  | 82.1     | 63.2     |
|   | 52-9    | NC             | 180 | 150 | 170               | 180              | 180                | 180 | 180 | 180       | 180 | 180 | 180                    | 4.346    | 1.859  | 85.5      | 72.4    | 4.346    | 1.859  | 85.5     | 72.4     |
|   | 52-10   | NC             | 180 | 150 | 170               | 180              | 180                | 180 | 180 | 180       | 180 | 180 | 180                    | 5.148    | 2.353  | 59.7      | 85.8    | 5.148    | 2.353  | 59.7     | 85.8     |
| Grace Grade 59<br>Silica Gel<br>After Heat Aging<br>for 8 Hrs. at 300°C | 53-0    | NC             | 180 | 150 | 170               | 180              | 180                | 180 | 180 | 180       | 180 | 180 | 180                    | 1.576    | 0.3369 | 47.1      | 52.5    | 1.576    | 0.3369 | 47.1     | 52.5     |
|   | 53-1    | NC             | 180 | 150 | 170               | 180              | 180                | 180 | 180 | 180       | 180 | 180 | 180                    | 2.106    | 0.637  | 69.2      | 70.2    | 2.106    | 0.637  | 69.2     | 70.2     |
|   | 53-2    | NC             | 180 | 150 | 170               | 180              | 180                | 180 | 180 | 180       | 180 | 180 | 180                    | 2.631    | 0.599  | 69.3      | 49.5    | 2.631    | 0.599  | 69.3     | 49.5     |
|   | 53-3    | NC             | 180 | 150 | 170               | 180              | 180                | 180 | 180 | 180       | 180 | 180 | 180                    | 3.408    | 0.979  | 57.5      | 56.8    | 3.408    | 0.979  | 57.5     | 56.8     |
|   | 53-4    | NC             | 180 | 150 | 170               | 180              | 180                | 180 | 180 | 180       | 180 | 180 | 180                    | 3.773    | 1.063  | 57.0      | 62.2    | 3.773    | 1.063  | 57.0     | 62.2     |
| Grace Grade 59<br>Silica Gel<br>After Heat Aging<br>for 8 Hrs. at 300°C | 54-0    | NC             | 180 | 150 | 170               | 180              | 180                | 180 | 180 | 180       | 180 | 180 | 180                    | 2.222    | 0.6284 | 2.6       | 37.8    | 2.222    | 0.6284 | 2.6      | 37.8     |
|   | 54-1    | NC             | 180 | 150 | 170               | 180              | 180                | 180 | 180 | 180       | 180 | 180 | 180                    | 3.533    | 0.730  | 41.7      | 58.8    | 3.533    | 0.730  | 41.7     | 58.8     |
|   | 54-2    | NC             | 180 | 150 | 170               | 180              | 180                | 180 | 180 | 180       | 180 | 180 | 180                    | 3.553    | 0.654  | 37.1      | 58.8    | 3.553    | 0.654  | 37.1     | 58.8     |
|   | 54-3    | NC             | 180 | 150 | 170               | 180              | 180                | 180 | 180 | 180       | 180 | 180 | 180                    | 2.333    | 0.6275 | 40.9      | 38.3    | 2.333    | 0.6275 | 40.9     | 38.3     |
|   | 54-4    | NC             | 180 | 150 | 170               | 180              | 180                | 180 | 180 | 180       | 180 | 180 | 180                    | 3.776    | 1.2152 | 46.9      | 46.9    | 3.776    | 1.2152 | 46.9     | 46.9     |
| Grace 59 Silica Gel<br>After Heat Aging<br>for 8 Hrs. at 300°C          | 55-0    | NC             | 180 | 150 | 170               | 180              | 180                | 180 | 180 | 180       | 180 | 180 | 180                    | 3.868    | 1.071  | 52.1      | 63.5    | 3.868    | 1.071  | 52.1     | 63.5     |
|   | 55-1    | NC             | 180 | 150 | 170               | 180              | 180                | 180 | 180 | 180       | 180 | 180 | 180                    | 4.425    | 1.013  | 77.4      | 73.6    | 4.425    | 1.013  | 77.4     | 73.6     |
|   | 55-2    | NC             | 180 | 150 | 170               | 180              | 180                | 180 | 180 | 180       | 180 | 180 | 180                    | 2.276    | 0.410  | 36.4      | 37.5    | 2.276    | 0.410  | 36.4     | 37.5     |
|   | 55-3    | NC             | 180 | 150 | 170               | 180              | 180                | 180 | 180 | 180       | 180 | 180 | 180                    | 3.416    | 0.844  | 53.1      | 52.9    | 3.416    | 0.844  | 53.1     | 52.9     |
|   | 55-4    | NC             | 180 | 150 | 170               | 180              | 180                | 180 | 180 | 180       | 180 | 180 | 180                    | 4.217    | 1.623  | 76.5      | 69.2    | 4.217    | 1.623  | 76.5     | 69.2     |
| Grace 59 Silica Gel<br>After Heat Aging<br>for 8 Hrs. at 300°C          | 56-0    | NC             | 180 | 150 | 170               | 180              | 180                | 180 | 180 | 180       | 180 | 180 | 180                    | 2.468    | 2.01   | 86.1      | 72.8    | 2.468    | 2.01   | 86.1     | 72.8     |
|   | 56-1    | NC             | 180 | 150 | 170               | 180              | 180                | 180 | 180 | 180       | 180 | 180 | 180                    | 2.642    | 0.627  | 12.2      | 37.0    | 2.642    | 0.627  | 12.2     | 37.0     |
|   | 56-2    | NC             | 180 | 150 | 170               | 180              | 180                | 180 | 180 | 180       | 180 | 180 | 180                    | 2.648    | 0.627  | 12.2      | 37.0    | 2.648    | 0.627  | 12.2     | 37.0     |
|   | 56-3    | NC             | 180 | 150 | 170               | 180              | 180                | 180 | 180 | 180       | 180 | 180 | 180                    | 2.717    | 0.627  | 12.2      | 37.0    | 2.717    | 0.627  | 12.2     | 37.0     |
|   | 56-4    | NC             | 180 | 150 | 170               | 180              | 180                | 180 | 180 | 180       | 180 | 180 | 180                    | 2.717    | 0.627  | 12.2      | 37.0    | 2.717    | 0.627  | 12.2     | 37.0     |

TABLE III-3

LABORATORY BEAKER TESTS

Run #1 - X2121-36-1

Procedure - Added 10-15 grams dry silica gel (Grade grade 59) to 275 grams of molten AN/U at 300°F. (2/1 AN/U mole ratio)

- Hand stirred for ten minutes
- Allowed catalyst to settle
- Poured off melt
- Spread wet silica gel on paper towel.
- \* - (Dried at 165°F overnight)

Observations -

- Bubbling on first contact presumably due to venting of entrained air.
- Wet silica gel on paper towel was very soft. It fractured with the slightest touch.
- Estimated attrition was 5-10%.

Run #2 - X2121-37-1

Procedure - Same as X2121-36-1 except melt contained 5% liquid water.

Observations - Same as Run #1 but with a higher percentage of attrition (10-20%).

Run #3 - X2121-37-2

Procedure - Dropped dry silica gel (Grace grade 59) into boiling water (212°F).

- Stirred for ten minutes
- Allowed catalyst to settle
- Poured off water
- Spread wet silica gel on paper towel.

Observations -

- Bubbling on first contact presumably due to venting of entrained air.
- Wet silica gel was softer than the dry silica gel but much harder than recovered catalyst from Runs #1 and #2.
- Estimated attrition was less ( 5% ) than in the two previous runs.

TABLE III-3 (Continued)

Run #4 - X2121-38-1

Procedure - Dropped dry Houdry beads into a melt of AN/U as in Run #1.

Observations -

- Houdry beads floated on top of the melt for about five minutes before sinking. After sinking, the beads continued to release vented air for an additional 5-10 minutes.
- Recovered beads appeared to be harder than the original beads. There was no apparent catalyst attrition.

Run #5 - X2121-39-1

Procedure - Same as Run #1 but using preheated silica gel (350-400°F)

Observations - Same conclusions as noted for Run #3.

FOUR-INCH-DIAMETER REACTOR SUMMARY

(B)

| Date     | 1-29-73<br>7:30 P.M.<br>3 |                            | 1-29-73<br>10:30 P.M.<br>6 |                            | 1-30-73<br>1:00 A.M.<br>8.5 |                            | 1-30-73<br>1:00 P.M.<br>9.5 |                            | 1-30-73<br>4:30 P.M.<br>13 |                            |
|----------|---------------------------|----------------------------|----------------------------|----------------------------|-----------------------------|----------------------------|-----------------------------|----------------------------|----------------------------|----------------------------|
|          | Actual Feed               | Calo. Basis<br>Theor. Feed | Actual Feed                | Calo. Basis<br>Theor. Feed | Actual Feed                 | Calo. Basis<br>Theor. Feed | Actual Feed                 | Calo. Basis<br>Theor. Feed | Actual Feed                | Calo. Basis<br>Theor. Feed |
| Feed     | 30                        | 30                         | 30                         | 30                         | 30                          | 30                         | 35                          | 35                         | 35                         | 35                         |
| Reaction | -                         | -                          | -                          | -                          | -                           | -                          | -                           | -                          | -                          | -                          |
| Reaction | 27.3                      | 27.3                       | 26.2                       | 27.3                       | 26.2                        | 27.3                       | -                           | 27.3                       | -                          | 27.3                       |
| Reaction | 67.4                      | 72.7                       | 71.7                       | 72.7                       | 71.7                        | 72.7                       | -                           | 72.7                       | -                          | 72.7                       |
| Reaction | 23.4                      | -                          | 2.2                        | -                          | 2.2                         | -                          | -                           | -                          | -                          | -                          |
| Reaction | 0.6                       | -                          | 0.5                        | -                          | 0.5                         | -                          | -                           | -                          | -                          | -                          |
| Reaction | -                         | -                          | -                          | -                          | -                           | -                          | -                           | -                          | -                          | -                          |
| Reaction | 0.474                     | 0.455                      | 0.437                      | 0.455                      | 0.437                       | 0.455                      | 0.455                       | 0.455                      | 0.455                      | 0.455                      |
| Reaction | 0.866                     | 0.909                      | 0.896                      | 0.909                      | 0.896                       | 0.909                      | 0.909                       | 0.909                      | 0.909                      | 0.909                      |
| Reaction | 0.025                     | -                          | 0.018                      | -                          | 0.018                       | -                          | -                           | -                          | -                          | -                          |
| Reaction | 0.891                     | 0.909                      | 0.914                      | 0.909                      | 0.914                       | 0.909                      | 0.909                       | 0.909                      | 0.909                      | 0.909                      |
| Reaction | 0.531                     | 0.493                      | 0.479                      | 0.493                      | 0.479                       | 0.493                      | 0.493                       | 0.493                      | 0.493                      | 0.493                      |
| Reaction | 0.028                     | -                          | 0.020                      | -                          | 0.020                       | -                          | -                           | -                          | -                          | -                          |
| Reaction | 0.371                     | 0.338                      | 0.343                      | 0.338                      | 0.343                       | 0.338                      | 0.378                       | 0.378                      | 0.378                      | 0.378                      |
| Reaction | 0.158                     | 0.169                      | 0.191                      | 0.169                      | 0.191                       | 0.169                      | 0.185                       | 0.185                      | 0.185                      | 0.185                      |
| Reaction | 0.425                     | 0.550                      | 0.540                      | 0.550                      | 0.540                       | 0.550                      | 0.490                       | 0.490                      | 0.490                      | 0.490                      |
| Reaction | 85.0                      | 110.0                      | 102.0                      | 110.0                      | 102.0                       | 110.0                      | 98.0                        | 98.0                       | 98.0                       | 98.0                       |
| Reaction | 0.172                     | 0.206                      | 0.213                      | 0.206                      | 0.213                       | 0.206                      | 0.205                       | 0.205                      | 0.205                      | 0.205                      |
| Reaction | 5.16                      | 6.2                        | 6.4                        | 6.2                        | 6.4                         | 6.2                        | 7.2                         | 7.2                        | 7.2                        | 7.2                        |

TABLE III-4 (Continued)

(b)

Basis: 1. One Reactor (R-200)  
 2. Houdry Macroporous Silica Beads  
 3. Hercules' Donora Reagent Grade AN, Olin U  
 4. Recycle - None

| 1. Date<br>2. Time<br>3. Elapsed Feed Time (hrs.)   | 1-30-73<br>7:30 P.M.<br>16 |       |         |  | 1-30-73<br>10:30 P.M.<br>19 |       |         |  | 1-31-73<br>1:30 A.M.<br>22 |       |         |   | 1-31-73<br>4:30 A.M.<br>25 |       |         |   | 1-31-73<br>7:30 A.M.<br>28 |       |         |  |
|---|----------------------------|-------|---------|--|-----------------------------|-------|---------|--|----------------------------|-------|---------|---|----------------------------|-------|---------|---|----------------------------|-------|---------|--|
|   | Feed                       |       | Reactor |  | Feed                        |       | Reactor |  | Feed                       |       | Reactor |   | Feed                       |       | Reactor |   | Feed                       |       | Reactor |  |
|   | Actual                     | Theo. | Melt    |  | Actual                      | Theo. | Melt    |  | Actual                     | Theo. | Melt    |   | Actual                     | Theo. | Melt    |   | Actual                     | Theo. | Melt    |  |
| 4. Rate (lbs/hr.)   | 35                         | 35    | -       |  | 35                          | 35    | -       |  | -                          | 35    | 35      | - | -                          | 35    | 35      | - | 35                         | 35    | -       |  |
| 5. Analysis (%)   |                            |       |         |  |                             |       |         |  |                            |       |         |   |                            |       |         |   |                            |       |         |  |
| a. C  | 22.0                       | 27.3  | 4.4     |  | 27.3                        | 72.7  | 5.9     |  | -                          | 27.3  | 4.7     |   | -                          | 27.3  | 5.4     |   | 26.7                       | 27.3  | 6.0     |  |
| b. AN   | 75.2                       | 72.7  | 69.7    |  | 72.7                        | -     | 70.1    |  | -                          | 72.7  | 65.6    |   | -                          | 72.7  | 70.2    |   | 69.7                       | 72.7  | 65.0    |  |
| c. GN   | 3.4                        | -     | 26.9    |  | -                           | -     | 24.8    |  | -                          | -     | 26.2    |   | -                          | -     | 24.8    |   | 2.4                        | -     | 29.4    |  |
| d. H <sub>2</sub> O   | 0.5                        |       |         |  |                             |       | -       |  |                            |       | -       |   |                            |       | -       |   | 0.5                        |       | -       |  |
| e. Insolubles   |                            |       |         |  |                             |       |         |  |                            |       |         |   |                            |       |         |   |                            |       |         |  |
| 6. Unit   | 0.367                      | 0.455 | 0.073   |  | 0.455                       | 0.098 | 0.098   |  | 0.455                      | 0.078 | 0.078   |   | 0.455                      | 0.090 | 0.090   |   | 0.445                      | 0.455 | 0.100   |  |
| 7. AN <sub>0</sub>  | 0.940                      | 0.909 | 0.872   |  | 0.909                       | 0.878 | 0.878   |  | 0.909                      | 0.872 | 0.872   |   | 0.909                      | 0.877 | 0.877   |   | 0.872                      | 0.909 | 0.818   |  |
| 8. GN <sub>0</sub>  | 0.028                      | -     | 0.220   |  | -                           | 0.208 | 0.214   |  | -                          | -     | 0.214   |   | -                          | -     | 0.203   |   | 0.019                      | -     | 0.241   |  |
| 9. AN <sub>1</sub>  | 0.968                      | 0.909 | 1.092   |  | 0.909                       | 1.081 | 1.081   |  | 0.909                      | 0.909 | 1.086   |   | 0.909                      | 0.909 | 1.080   |   | 0.891                      | 0.909 | 1.059   |  |
| 10. H <sub>2</sub> O <sub>1</sub>   | 0.379                      | 0.498 | 0.067   |  | 0.498                       | 0.096 | 0.096   |  | 0.498                      | 0.072 | 0.072   |   | 0.498                      | 0.498 | 0.083   |   | 0.499                      | 0.498 | 0.092   |  |
| 11. C <sub>0</sub> AN <sub>0</sub> N <sub>0</sub>   | 0.029                      | -     | 0.202   |  | -                           | 0.188 | 0.188   |  | -                          | -     | 0.197   |   | -                          | -     | 0.188   |   | 0.021                      | -     | 0.228   |  |
| 12. C <sub>1</sub> AN <sub>1</sub> N <sub>1</sub>   |                            |       |         |  |                             |       |         |  |                            |       |         |   |                            |       |         |   |                            |       |         |  |
| 13. C <sub>0</sub> AN <sub>0</sub> N <sub>0</sub>   | 0.312                      |       | 0.431   |  |                             | 0.402 | 0.402   |  |                            |       |         |   |                            |       |         |   | 0.407                      |       | 0.406   |  |
| 14. C <sub>1</sub> AN <sub>1</sub> N <sub>1</sub>   | 0.173                      |       | 0.202   |  |                             | 0.188 | 0.188   |  |                            |       |         |   |                            |       |         |   | 0.207                      |       | 0.228   |  |
| 15. C <sub>0</sub> AN <sub>0</sub> N <sub>0</sub>   | 0.555                      |       | 0.470   |  |                             | 0.466 | 0.466   |  |                            |       |         |   |                            |       |         |   | 0.509                      |       | 0.561   |  |
| 16. C <sub>1</sub> AN <sub>1</sub> N <sub>1</sub>   | 111.0                      |       | 94.0    |  |                             | 93.2  | 93.2    |  |                            |       |         |   |                            |       |         |   | 101.8                      |       | 112.2   |  |
| 17. C <sub>0</sub> AN <sub>0</sub> N <sub>0</sub>   | 0.204                      |       | 0.223   |  |                             | 0.208 | 0.208   |  |                            |       |         |   |                            |       |         |   | 0.225                      |       | 0.253   |  |
| 18. C <sub>1</sub> AN <sub>1</sub> N <sub>1</sub>   | 7.1                        |       | 7.8     |  |                             | 7.26  | 7.26    |  |                            |       |         |   |                            |       |         |   | 7.9                        |       | 8.9     |  |
| 19. Properties (lb. GN/lb. Feed)<br>20. Properties (lb. GN/lb. Feed)<br>21. Properties (lb. GN/lb. Feed)<br>22. Properties (lb. GN/lb. Feed)<br>23. Properties (lb. GN/lb. Feed)<br>24. Properties (lb. GN/lb. Feed)<br>25. Properties (lb. GN/lb. Feed)<br>26. Properties (lb. GN/lb. Feed)<br>27. Properties (lb. GN/lb. Feed)<br>28. Properties (lb. GN/lb. Feed)<br>29. Properties (lb. GN/lb. Feed)<br>30. Properties (lb. GN/lb. Feed)<br>31. Properties (lb. GN/lb. Feed)<br>32. Properties (lb. GN/lb. Feed)<br>33. Properties (lb. GN/lb. Feed)<br>34. Properties (lb. GN/lb. Feed)<br>35. Properties (lb. GN/lb. Feed)<br>36. Properties (lb. GN/lb. Feed)<br>37. Properties (lb. GN/lb. Feed)<br>38. Properties (lb. GN/lb. Feed)<br>39. Properties (lb. GN/lb. Feed)<br>40. Properties (lb. GN/lb. Feed)<br>41. Properties (lb. GN/lb. Feed)<br>42. Properties (lb. GN/lb. Feed)<br>43. Properties (lb. GN/lb. Feed)<br>44. Properties (lb. GN/lb. Feed)<br>45. Properties (lb. GN/lb. Feed)<br>46. Properties (lb. GN/lb. Feed)<br>47. Properties (lb. GN/lb. Feed)<br>48. Properties (lb. GN/lb. Feed)<br>49. Properties (lb. GN/lb. Feed)<br>50. Properties (lb. GN/lb. Feed)<br>51. Properties (lb. GN/lb. Feed)<br>52. Properties (lb. GN/lb. Feed)<br>53. Properties (lb. GN/lb. Feed)<br>54. Properties (lb. GN/lb. Feed)<br>55. Properties (lb. GN/lb. Feed)<br>56. Properties (lb. GN/lb. Feed)<br>57. Properties (lb. GN/lb. Feed)<br>58. Properties (lb. GN/lb. Feed)<br>59. Properties (lb. GN/lb. Feed)<br>60. Properties (lb. GN/lb. Feed)<br>61. Properties (lb. GN/lb. Feed)<br>62. Properties (lb. GN/lb. Feed)<br>63. Properties (lb. GN/lb. Feed)<br>64. Properties (lb. GN/lb. Feed)<br>65. Properties (lb. GN/lb. Feed)<br>66. Properties (lb. GN/lb. Feed)<br>67. Properties (lb. GN/lb. Feed)<br>68. Properties (lb. GN/lb. Feed)<br>69. Properties (lb. GN/lb. Feed)<br>70. Properties (lb. GN/lb. Feed)<br>71. Properties (lb. GN/lb. Feed)<br>72. Properties (lb. GN/lb. Feed)<br>73. Properties (lb. GN/lb. Feed)<br>74. Properties (lb. GN/lb. Feed)<br>75. Properties (lb. GN/lb. Feed)<br>76. Properties (lb. GN/lb. Feed)<br>77. Properties (lb. GN/lb. Feed)<br>78. Properties (lb. GN/lb. Feed)<br>79. Properties (lb. GN/lb. Feed)<br>80. Properties (lb. GN/lb. Feed)<br>81. Properties (lb. GN/lb. Feed)<br>82. Properties (lb. GN/lb. Feed)<br>83. Properties (lb. GN/lb. Feed)<br>84. Properties (lb. GN/lb. Feed)<br>85. Properties (lb. GN/lb. Feed)<br>86. Properties (lb. GN/lb. Feed)<br>87. Properties (lb. GN/lb. Feed)<br>88. Properties (lb. GN/lb. Feed)<br>89. Properties (lb. GN/lb. Feed)<br>90. Properties (lb. GN/lb. Feed)<br>91. Properties (lb. GN/lb. Feed)<br>92. Properties (lb. GN/lb. Feed)<br>93. Properties (lb. GN/lb. Feed)<br>94. Properties (lb. GN/lb. Feed)<br>95. Properties (lb. GN/lb. Feed)<br>96. Properties (lb. GN/lb. Feed)<br>97. Properties (lb. GN/lb. Feed)<br>98. Properties (lb. GN/lb. Feed)<br>99. Properties (lb. GN/lb. Feed)<br>100. Properties (lb. GN/lb. Feed) |                            |       |         |  |                             |       |         |  |                            |       |         |   |                            |       |         |   |                            |       |         |  |



TABLE III-4 (Continued)

(d)

Basis: 1. One Reactor (R-200)

2. Houdry Macroporous Silica Beds

3. Hercules' Donora Reagent Grade AN, Olin U

4. Recycle - None

|                   | 2-1-73<br>1:00 A.M.<br>45.5 |             | 2-1-73<br>1:30 P.M.<br>48 |             | 2-1-73<br>10:30 P.M.<br>51 |             | 2-2-73<br>1:30 A.M.<br>54 |             | 2-2-73<br>4:30 A.M.<br>57 |             |
|-------------------|-----------------------------|-------------|---------------------------|-------------|----------------------------|-------------|---------------------------|-------------|---------------------------|-------------|
|                   | Feed<br>Actual              | Theo.<br>27 | Feed<br>Actual            | Theo.<br>27 | Feed<br>Actual             | Theo.<br>27 | Feed<br>Actual            | Theo.<br>27 | Feed<br>Actual            | Theo.<br>25 |
| 1. Reactor Melt   |                             |             |                           |             |                            |             |                           |             |                           |             |
| 2. Reactor Melt   |                             |             |                           |             |                            |             |                           |             |                           |             |
| 3. Reactor Melt   |                             |             |                           |             |                            |             |                           |             |                           |             |
| 4. Reactor Melt   |                             |             |                           |             |                            |             |                           |             |                           |             |
| 5. Reactor Melt   |                             |             |                           |             |                            |             |                           |             |                           |             |
| 6. Reactor Melt   |                             |             |                           |             |                            |             |                           |             |                           |             |
| 7. Reactor Melt   |                             |             |                           |             |                            |             |                           |             |                           |             |
| 8. Reactor Melt   |                             |             |                           |             |                            |             |                           |             |                           |             |
| 9. Reactor Melt   |                             |             |                           |             |                            |             |                           |             |                           |             |
| 10. Reactor Melt  |                             |             |                           |             |                            |             |                           |             |                           |             |
| 11. Reactor Melt  |                             |             |                           |             |                            |             |                           |             |                           |             |
| 12. Reactor Melt  |                             |             |                           |             |                            |             |                           |             |                           |             |
| 13. Reactor Melt  |                             |             |                           |             |                            |             |                           |             |                           |             |
| 14. Reactor Melt  |                             |             |                           |             |                            |             |                           |             |                           |             |
| 15. Reactor Melt  |                             |             |                           |             |                            |             |                           |             |                           |             |
| 16. Reactor Melt  |                             |             |                           |             |                            |             |                           |             |                           |             |
| 17. Reactor Melt  |                             |             |                           |             |                            |             |                           |             |                           |             |
| 18. Reactor Melt  |                             |             |                           |             |                            |             |                           |             |                           |             |
| 19. Reactor Melt  |                             |             |                           |             |                            |             |                           |             |                           |             |
| 20. Reactor Melt  |                             |             |                           |             |                            |             |                           |             |                           |             |
| 21. Reactor Melt  |                             |             |                           |             |                            |             |                           |             |                           |             |
| 22. Reactor Melt  |                             |             |                           |             |                            |             |                           |             |                           |             |
| 23. Reactor Melt  |                             |             |                           |             |                            |             |                           |             |                           |             |
| 24. Reactor Melt  |                             |             |                           |             |                            |             |                           |             |                           |             |
| 25. Reactor Melt  |                             |             |                           |             |                            |             |                           |             |                           |             |
| 26. Reactor Melt  |                             |             |                           |             |                            |             |                           |             |                           |             |
| 27. Reactor Melt  |                             |             |                           |             |                            |             |                           |             |                           |             |
| 28. Reactor Melt  |                             |             |                           |             |                            |             |                           |             |                           |             |
| 29. Reactor Melt  |                             |             |                           |             |                            |             |                           |             |                           |             |
| 30. Reactor Melt  |                             |             |                           |             |                            |             |                           |             |                           |             |
| 31. Reactor Melt  |                             |             |                           |             |                            |             |                           |             |                           |             |
| 32. Reactor Melt  |                             |             |                           |             |                            |             |                           |             |                           |             |
| 33. Reactor Melt  |                             |             |                           |             |                            |             |                           |             |                           |             |
| 34. Reactor Melt  |                             |             |                           |             |                            |             |                           |             |                           |             |
| 35. Reactor Melt  |                             |             |                           |             |                            |             |                           |             |                           |             |
| 36. Reactor Melt  |                             |             |                           |             |                            |             |                           |             |                           |             |
| 37. Reactor Melt  |                             |             |                           |             |                            |             |                           |             |                           |             |
| 38. Reactor Melt  |                             |             |                           |             |                            |             |                           |             |                           |             |
| 39. Reactor Melt  |                             |             |                           |             |                            |             |                           |             |                           |             |
| 40. Reactor Melt  |                             |             |                           |             |                            |             |                           |             |                           |             |
| 41. Reactor Melt  |                             |             |                           |             |                            |             |                           |             |                           |             |
| 42. Reactor Melt  |                             |             |                           |             |                            |             |                           |             |                           |             |
| 43. Reactor Melt  |                             |             |                           |             |                            |             |                           |             |                           |             |
| 44. Reactor Melt  |                             |             |                           |             |                            |             |                           |             |                           |             |
| 45. Reactor Melt  |                             |             |                           |             |                            |             |                           |             |                           |             |
| 46. Reactor Melt  |                             |             |                           |             |                            |             |                           |             |                           |             |
| 47. Reactor Melt  |                             |             |                           |             |                            |             |                           |             |                           |             |
| 48. Reactor Melt  |                             |             |                           |             |                            |             |                           |             |                           |             |
| 49. Reactor Melt  |                             |             |                           |             |                            |             |                           |             |                           |             |
| 50. Reactor Melt  |                             |             |                           |             |                            |             |                           |             |                           |             |
| 51. Reactor Melt  |                             |             |                           |             |                            |             |                           |             |                           |             |
| 52. Reactor Melt  |                             |             |                           |             |                            |             |                           |             |                           |             |
| 53. Reactor Melt  |                             |             |                           |             |                            |             |                           |             |                           |             |
| 54. Reactor Melt  |                             |             |                           |             |                            |             |                           |             |                           |             |
| 55. Reactor Melt  |                             |             |                           |             |                            |             |                           |             |                           |             |
| 56. Reactor Melt  |                             |             |                           |             |                            |             |                           |             |                           |             |
| 57. Reactor Melt  |                             |             |                           |             |                            |             |                           |             |                           |             |
| 58. Reactor Melt  |                             |             |                           |             |                            |             |                           |             |                           |             |
| 59. Reactor Melt  |                             |             |                           |             |                            |             |                           |             |                           |             |
| 60. Reactor Melt  |                             |             |                           |             |                            |             |                           |             |                           |             |
| 61. Reactor Melt  |                             |             |                           |             |                            |             |                           |             |                           |             |
| 62. Reactor Melt  |                             |             |                           |             |                            |             |                           |             |                           |             |
| 63. Reactor Melt  |                             |             |                           |             |                            |             |                           |             |                           |             |
| 64. Reactor Melt  |                             |             |                           |             |                            |             |                           |             |                           |             |
| 65. Reactor Melt  |                             |             |                           |             |                            |             |                           |             |                           |             |
| 66. Reactor Melt  |                             |             |                           |             |                            |             |                           |             |                           |             |
| 67. Reactor Melt  |                             |             |                           |             |                            |             |                           |             |                           |             |
| 68. Reactor Melt  |                             |             |                           |             |                            |             |                           |             |                           |             |
| 69. Reactor Melt  |                             |             |                           |             |                            |             |                           |             |                           |             |
| 70. Reactor Melt  |                             |             |                           |             |                            |             |                           |             |                           |             |
| 71. Reactor Melt  |                             |             |                           |             |                            |             |                           |             |                           |             |
| 72. Reactor Melt  |                             |             |                           |             |                            |             |                           |             |                           |             |
| 73. Reactor Melt  |                             |             |                           |             |                            |             |                           |             |                           |             |
| 74. Reactor Melt  |                             |             |                           |             |                            |             |                           |             |                           |             |
| 75. Reactor Melt  |                             |             |                           |             |                            |             |                           |             |                           |             |
| 76. Reactor Melt  |                             |             |                           |             |                            |             |                           |             |                           |             |
| 77. Reactor Melt  |                             |             |                           |             |                            |             |                           |             |                           |             |
| 78. Reactor Melt  |                             |             |                           |             |                            |             |                           |             |                           |             |
| 79. Reactor Melt  |                             |             |                           |             |                            |             |                           |             |                           |             |
| 80. Reactor Melt  |                             |             |                           |             |                            |             |                           |             |                           |             |
| 81. Reactor Melt  |                             |             |                           |             |                            |             |                           |             |                           |             |
| 82. Reactor Melt  |                             |             |                           |             |                            |             |                           |             |                           |             |
| 83. Reactor Melt  |                             |             |                           |             |                            |             |                           |             |                           |             |
| 84. Reactor Melt  |                             |             |                           |             |                            |             |                           |             |                           |             |
| 85. Reactor Melt  |                             |             |                           |             |                            |             |                           |             |                           |             |
| 86. Reactor Melt  |                             |             |                           |             |                            |             |                           |             |                           |             |
| 87. Reactor Melt  |                             |             |                           |             |                            |             |                           |             |                           |             |
| 88. Reactor Melt  |                             |             |                           |             |                            |             |                           |             |                           |             |
| 89. Reactor Melt  |                             |             |                           |             |                            |             |                           |             |                           |             |
| 90. Reactor Melt  |                             |             |                           |             |                            |             |                           |             |                           |             |
| 91. Reactor Melt  |                             |             |                           |             |                            |             |                           |             |                           |             |
| 92. Reactor Melt  |                             |             |                           |             |                            |             |                           |             |                           |             |
| 93. Reactor Melt  |                             |             |                           |             |                            |             |                           |             |                           |             |
| 94. Reactor Melt  |                             |             |                           |             |                            |             |                           |             |                           |             |
| 95. Reactor Melt  |                             |             |                           |             |                            |             |                           |             |                           |             |
| 96. Reactor Melt  |                             |             |                           |             |                            |             |                           |             |                           |             |
| 97. Reactor Melt  |                             |             |                           |             |                            |             |                           |             |                           |             |
| 98. Reactor Melt  |                             |             |                           |             |                            |             |                           |             |                           |             |
| 99. Reactor Melt  |                             |             |                           |             |                            |             |                           |             |                           |             |
| 100. Reactor Melt |                             |             |                           |             |                            |             |                           |             |                           |             |

Used 10:30 P.M., 2/1/73 feed analysis



TABLE III-4 (Continued)

(e)

Basis: 1. One Reactor (R-200)  
 2. Houdry Macroporous Silica Beds  
 3. Hercules' Donora Reagent Grade AN, Olin U  
 4. Recycle - None

| 1. Date<br>2. Time<br>3. elapsed feed time (hrs) | 2-2-72<br>7:30 A. M.<br>60 |       | 2-2-73<br>10:30 A. M.<br>63 |       | 2-2-73<br>1:30 P. M.<br>66 |       | 2-2-73<br>7:30 P. M.<br>72 |       | 2-2-73<br>10:30 P. M.<br>75 |       |
|--|----------------------------|-------|-----------------------------|-------|----------------------------|-------|----------------------------|-------|-----------------------------|-------|
|  | Feed                       |       | Feed                        |       | Feed                       |       | Feed                       |       | Feed                        |       |
|  | Actual                     | Theo. | Actual                      | Theo. | Actual                     | Theo. | Actual                     | Theo. | Actual                      | Theo. |
| 4. Rate (lb. feed)<br>a. Analysis (%)            | 29                         | 29    | 30                          | 30    | 30                         | 30    | 30                         | 30    | 27.5                        | 27.5  |
| b. U   | -                          | 42.9  | -                           | 42.9  | -                          | 42.9  | 40.0                       | 42.9  | 40.0                        | 42.9  |
| c. AN  | -                          | 57.1  | -                           | 57.1  | -                          | 57.1  | 55.3                       | 57.1  | 55.4                        | 57.1  |
| d. GN  | -                          | -     | -                           | -     | -                          | -     | 2.4                        | -     | 4.7                         | -     |
| e. H <sub>2</sub> O                              | -                          | -     | -                           | -     | -                          | -     | 1.5                        | -     | 1.5                         | -     |
| f. Insolubles                                    | -                          | -     | -                           | -     | -                          | -     | -                          | -     | -                           | -     |
| 5. Unit  | 0.350                      | 0.350 | 0.350                       | 0.350 | 0.350                      | 0.350 | 0.350                      | 0.350 | 0.350                       | 0.350 |
| 6. ANs   | 0.715                      | 0.715 | 0.715                       | 0.715 | 0.715                      | 0.715 | 0.667                      | 0.715 | 0.667                       | 0.715 |
| 7. GNs   | 0.715                      | 0.715 | 0.715                       | 0.715 | 0.715                      | 0.715 | 0.691                      | 0.715 | 0.693                       | 0.715 |
| 8. N <sub>2</sub>                                | -                          | -     | -                           | -     | -                          | -     | 0.020                      | -     | 0.039                       | -     |
| 9. H <sub>2</sub> O                              | 0.715                      | 0.715 | 0.715                       | 0.715 | 0.715                      | 0.715 | 0.711                      | 0.715 | 0.732                       | 0.715 |
| 10. Total  | 1.000                      | 1.000 | 1.000                       | 1.000 | 1.000                      | 1.000 | 0.938                      | 1.000 | 0.910                       | 1.000 |
| 11. Calc. Basis                                  | -                          | -     | -                           | -     | -                          | -     | 0.028                      | -     | 0.053                       | -     |
| 12. Actual Feed                                  | -                          | -     | -                           | -     | -                          | -     | 0.649                      | -     | 0.739                       | -     |
| 13. Calc. Basis                                  | 0.884                      | 0.884 | 0.834                       | 0.834 | 0.821                      | 0.821 | 0.333                      | 0.352 | 0.403                       | 0.403 |
| 14. ANs  | 0.432                      | 0.432 | 0.402                       | 0.402 | 0.389                      | 0.389 | 0.515                      | 0.476 | 0.487                       | 0.487 |
| 15. GNs  | 0.486                      | 0.486 | 0.483                       | 0.483 | 0.473                      | 0.473 | 103.0                      | 95.2  | 97.4                        | 97.4  |
| 16. H <sub>2</sub> O                             | 97.8                       | 97.8  | 96.6                        | 96.6  | 94.6                       | 94.6  | 0.289                      | 0.309 | 0.314                       | 0.352 |
| 17. Total  | 0.377                      | 0.377 | 0.351                       | 0.351 | 0.338                      | 0.338 | 8.7                        | 9.3   | 8.7                         | 9.7   |
| 18. Reactor Melt                                 | 10.5                       | 10.5  | 10.5                        | 10.5  | 10.2                       | 10.2  | -                          | -     | -                           | -     |
| 19. Reactor Melt                                 | -                          | -     | -                           | -     | -                          | -     | -                          | -     | -                           | -     |
| 20. Reactor Yield                                | -                          | -     | -                           | -     | -                          | -     | -                          | -     | -                           | -     |

TABLE III-4 (Continued)

(F)

Basis: 1. One Reactor (R-200)  
 2. Houdry Macroporous Silica Beads  
 3. Hercules' Donora Reagent Grade AN, Olin U  
 4. Recycle - None

| 1. Date<br>2. Time<br>3. Elapsed Time (hrs) | 2-3-73<br>4:30 A.M.<br>81 |               | 2-3-73<br>7:30 A.M.<br>84 |               | 2-3-73<br>10:30 A.M.<br>87 |               | 2-3-73<br>4:30 P.M.<br>93 |               | 2-3-73<br>10:30 P.M.<br>99 |               |
|---|---------------------------|---------------|---------------------------|---------------|----------------------------|---------------|---------------------------|---------------|----------------------------|---------------|
|   | Feed<br>Actual            | Feed<br>Theo. | Feed<br>Actual            | Feed<br>Theo. | Feed<br>Actual             | Feed<br>Theo. | Feed<br>Actual            | Feed<br>Theo. | Feed<br>Actual             | Feed<br>Theo. |
| 4. Reactor Melt                             | 17                        |               | 18                        |               | 18                         |               | 18                        |               | 18                         |               |
| 5. Reactor Melt                             | 11.3                      |               | 9.8                       |               | 8.9                        |               | 10.1                      |               | 10.7                       |               |
| 6. Reactor Melt                             | 44.1                      |               | 40.9                      |               | 45.7                       |               | 44.9                      |               | 43.9                       |               |
| 7. Reactor Melt                             | 43.7                      |               | 48.7                      |               | 45.6                       |               | 45.5                      |               | 44.5                       |               |
| 8. Reactor Melt                             | -                         |               | -                         |               | -                          |               | -                         |               | -                          |               |
| 9. Reactor Melt                             | 0.390                     |               | 0.390                     |               | 0.396                      |               | 0.399                     |               | 0.400                      |               |
| 10. Reactor Melt                            | 0.715                     |               | 0.715                     |               | 0.715                      |               | 0.715                     |               | 0.715                      |               |
| 11. Reactor Melt                            | 0.551                     |               | 0.511                     |               | 0.571                      |               | 0.561                     |               | 0.549                      |               |
| 12. Reactor Melt                            | 0.358                     |               | 0.400                     |               | 0.374                      |               | 0.373                     |               | 0.365                      |               |
| 13. Reactor Melt                            | 0.909                     |               | 0.911                     |               | 0.945                      |               | 0.934                     |               | 0.914                      |               |
| 14. Reactor Melt                            | 0.208                     |               | 0.179                     |               | 0.156                      |               | 0.180                     |               | 0.195                      |               |
| 15. Reactor Melt                            | 0.324                     |               | 0.439                     |               | 0.396                      |               | 0.399                     |               | 0.400                      |               |
| 16. Reactor Melt                            | 0.715                     |               | 0.715                     |               | 0.715                      |               | 0.715                     |               | 0.715                      |               |
| 17. Reactor Melt                            | 0.715                     |               | 0.715                     |               | 0.715                      |               | 0.715                     |               | 0.715                      |               |
| 18. Reactor Melt                            | 1.000                     |               | 1.000                     |               | 1.000                      |               | 1.000                     |               | 1.000                      |               |
| 19. Reactor Melt                            | -                         |               | -                         |               | -                          |               | -                         |               | -                          |               |
| 20. Reactor Melt                            | 0.806                     |               | 0.806                     |               | 0.806                      |               | 0.806                     |               | 0.806                      |               |
| 21. Reactor Melt                            | 0.375                     |               | 0.375                     |               | 0.375                      |               | 0.375                     |               | 0.375                      |               |
| 22. Reactor Melt                            | 0.459                     |               | 0.459                     |               | 0.459                      |               | 0.459                     |               | 0.459                      |               |
| 23. Reactor Melt                            | 0.322                     |               | 0.322                     |               | 0.322                      |               | 0.322                     |               | 0.322                      |               |
| 24. Reactor Melt                            | 0.322                     |               | 0.322                     |               | 0.322                      |               | 0.322                     |               | 0.322                      |               |
| 25. Reactor Melt                            | 0.322                     |               | 0.322                     |               | 0.322                      |               | 0.322                     |               | 0.322                      |               |
| 26. Reactor Melt                            | 0.322                     |               | 0.322                     |               | 0.322                      |               | 0.322                     |               | 0.322                      |               |
| 27. Reactor Melt                            | 0.322                     |               | 0.322                     |               | 0.322                      |               | 0.322                     |               | 0.322                      |               |
| 28. Reactor Melt                            | 0.322                     |               | 0.322                     |               | 0.322                      |               | 0.322                     |               | 0.322                      |               |
| 29. Reactor Melt                            | 0.322                     |               | 0.322                     |               | 0.322                      |               | 0.322                     |               | 0.322                      |               |
| 30. Reactor Melt                            | 0.322                     |               | 0.322                     |               | 0.322                      |               | 0.322                     |               | 0.322                      |               |
| 31. Reactor Melt                            | 0.322                     |               | 0.322                     |               | 0.322                      |               | 0.322                     |               | 0.322                      |               |
| 32. Reactor Melt                            | 0.322                     |               | 0.322                     |               | 0.322                      |               | 0.322                     |               | 0.322                      |               |
| 33. Reactor Melt                            | 0.322                     |               | 0.322                     |               | 0.322                      |               | 0.322                     |               | 0.322                      |               |
| 34. Reactor Melt                            | 0.322                     |               | 0.322                     |               | 0.322                      |               | 0.322                     |               | 0.322                      |               |
| 35. Reactor Melt                            | 0.322                     |               | 0.322                     |               | 0.322                      |               | 0.322                     |               | 0.322                      |               |
| 36. Reactor Melt                            | 0.322                     |               | 0.322                     |               | 0.322                      |               | 0.322                     |               | 0.322                      |               |
| 37. Reactor Melt                            | 0.322                     |               | 0.322                     |               | 0.322                      |               | 0.322                     |               | 0.322                      |               |
| 38. Reactor Melt                            | 0.322                     |               | 0.322                     |               | 0.322                      |               | 0.322                     |               | 0.322                      |               |
| 39. Reactor Melt                            | 0.322                     |               | 0.322                     |               | 0.322                      |               | 0.322                     |               | 0.322                      |               |
| 40. Reactor Melt                            | 0.322                     |               | 0.322                     |               | 0.322                      |               | 0.322                     |               | 0.322                      |               |
| 41. Reactor Melt                            | 0.322                     |               | 0.322                     |               | 0.322                      |               | 0.322                     |               | 0.322                      |               |
| 42. Reactor Melt                            | 0.322                     |               | 0.322                     |               | 0.322                      |               | 0.322                     |               | 0.322                      |               |
| 43. Reactor Melt                            | 0.322                     |               | 0.322                     |               | 0.322                      |               | 0.322                     |               | 0.322                      |               |
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| 45. Reactor Melt                            | 0.322                     |               | 0.322                     |               | 0.322                      |               | 0.322                     |               | 0.322                      |               |
| 46. Reactor Melt                            | 0.322                     |               | 0.322                     |               | 0.322                      |               | 0.322                     |               | 0.322                      |               |
| 47. Reactor Melt                            | 0.322                     |               | 0.322                     |               | 0.322                      |               | 0.322                     |               | 0.322                      |               |
| 48. Reactor Melt                            | 0.322                     |               | 0.322                     |               | 0.322                      |               | 0.322                     |               | 0.322                      |               |
| 49. Reactor Melt                            | 0.322                     |               | 0.322                     |               | 0.322                      |               | 0.322                     |               | 0.322                      |               |
| 50. Reactor Melt                            | 0.322                     |               | 0.322                     |               | 0.322                      |               | 0.322                     |               | 0.322                      |               |
| 51. Reactor Melt                            | 0.322                     |               | 0.322                     |               | 0.322                      |               | 0.322                     |               | 0.322                      |               |
| 52. Reactor Melt                            | 0.322                     |               | 0.322                     |               | 0.322                      |               | 0.322                     |               | 0.322                      |               |
| 53. Reactor Melt                            | 0.322                     |               | 0.322                     |               | 0.322                      |               | 0.322                     |               | 0.322                      |               |
| 54. Reactor Melt                            | 0.322                     |               | 0.322                     |               | 0.322                      |               | 0.322                     |               | 0.322                      |               |
| 55. Reactor Melt                            | 0.322                     |               | 0.322                     |               | 0.322                      |               | 0.322                     |               | 0.322                      |               |
| 56. Reactor Melt                            | 0.322                     |               | 0.322                     |               | 0.322                      |               | 0.322                     |               | 0.322                      |               |
| 57. Reactor Melt                            | 0.322                     |               | 0.322                     |               | 0.322                      |               | 0.322                     |               | 0.322                      |               |
| 58. Reactor Melt                            | 0.322                     |               | 0.322                     |               | 0.322                      |               | 0.322                     |               | 0.322                      |               |
| 59. Reactor Melt                            | 0.322                     |               | 0.322                     |               | 0.322                      |               | 0.322                     |               | 0.322                      |               |
| 60. Reactor Melt                            | 0.322                     |               | 0.322                     |               | 0.322                      |               | 0.322                     |               | 0.322                      |               |
| 61. Reactor Melt                            | 0.322                     |               | 0.322                     |               | 0.322                      |               | 0.322                     |               | 0.322                      |               |
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| 68. Reactor Melt                            | 0.322                     |               | 0.322                     |               | 0.322                      |               | 0.322                     |               | 0.322                      |               |
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| 71. Reactor Melt                            | 0.322                     |               | 0.322                     |               | 0.322                      |               | 0.322                     |               | 0.322                      |               |
| 72. Reactor Melt                            | 0.322                     |               | 0.322                     |               | 0.322                      |               | 0.322                     |               | 0.322                      |               |
| 73. Reactor Melt                            | 0.322                     |               | 0.322                     |               | 0.322                      |               | 0.322                     |               | 0.322                      |               |
| 74. Reactor Melt                            | 0.322                     |               | 0.322                     |               | 0.322                      |               | 0.322                     |               | 0.322                      |               |
| 75. Reactor Melt                            | 0.322                     |               | 0.322                     |               | 0.322                      |               | 0.322                     |               | 0.322                      |               |
| 76. Reactor Melt                            | 0.322                     |               | 0.322                     |               | 0.322                      |               | 0.322                     |               | 0.322                      |               |
| 77. Reactor Melt                            | 0.322                     |               | 0.322                     |               | 0.322                      |               | 0.322                     |               | 0.322                      |               |
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| 79. Reactor Melt                            | 0.322                     |               | 0.322                     |               | 0.322                      |               | 0.322                     |               | 0.322                      |               |
| 80. Reactor Melt                            | 0.322                     |               | 0.322                     |               | 0.322                      |               | 0.322                     |               | 0.322                      |               |
| 81. Reactor Melt                            | 0.322                     |               | 0.322                     |               | 0.322                      |               | 0.322                     |               | 0.322                      |               |
| 82. Reactor Melt                            | 0.322                     |               | 0.322                     |               | 0.322                      |               | 0.322                     |               | 0.322                      |               |
| 83. Reactor Melt                            | 0.322                     |               | 0.322                     |               | 0.322                      |               | 0.322                     |               | 0.322                      |               |
| 84. Reactor Melt                            | 0.322                     |               | 0.322                     |               | 0.322                      |               | 0.322                     |               | 0.322                      |               |
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| 87. Reactor Melt                            | 0.322                     |               | 0.322                     |               | 0.322                      |               | 0.322                     |               | 0.322                      |               |
| 88. Reactor Melt                            | 0.322                     |               | 0.322                     |               | 0.322                      |               | 0.322                     |               | 0.322                      |               |
| 89. Reactor Melt                            | 0.322                     |               | 0.322                     |               | 0.322                      |               | 0.322                     |               | 0.322                      |               |
| 90. Reactor Melt                            | 0.322                     |               | 0.322                     |               | 0.322                      |               | 0.322                     |               | 0.322                      |               |
| 91. Reactor Melt                            | 0.322                     |               | 0.322                     |               | 0.322                      |               | 0.322                     |               | 0.322                      |               |
| 92. Reactor Melt                            | 0.322                     |               | 0.322                     |               | 0.322                      |               | 0.322                     |               | 0.322                      |               |
| 93. Reactor Melt                            | 0.322                     |               | 0.322                     |               | 0.322                      |               | 0.322                     |               | 0.322                      |               |
| 94. Reactor Melt                            | 0.322                     |               | 0.322                     |               | 0.322                      |               | 0.322                     |               | 0.322                      |               |
| 95. Reactor Melt                            | 0.322                     |               | 0.322                     |               | 0.322                      |               | 0.322                     |               | 0.322                      |               |
| 96. Reactor Melt                            | 0.322                     |               | 0.322                     |               | 0.322                      |               | 0.322                     |               | 0.322                      |               |
| 97. Reactor Melt                            | 0.322                     |               | 0.322                     |               | 0.322                      |               | 0.322                     |               | 0.322                      |               |
| 98. Reactor Melt                            | 0.322                     |               | 0.322                     |               | 0.322                      |               | 0.322                     |               | 0.322                      |               |
| 99. Reactor Melt                            | 0.322                     |               | 0.322                     |               | 0.322                      |               | 0.322                     |               | 0.322                      |               |
| 100. Reactor Melt                           | 0.322                     |               | 0.322                     |               | 0.322                      |               | 0.322                     |               | 0.322                      |               |

TABLE III-4 (Continued)

Basics: 1. One Reactor (R-200)  
2. Houdry Macroporous Silica Beds  
3. Hercules' Donora Regent Grade AN, Olin U  
4. Recycle - None

[illegible]

APPENDIX IV

HAZA EVALUATION AND RISK CONTROL FOR KENVIL GUANIDINE NITRATE

(Reprint of Summary Report)

This is a final summary report on the work completed during Phases I through III of the Hazards Evaluation and Risk Control on the Kenvil pilot plant for the production of guanidine nitrate via the Boatwright-McKay-Roberts (BMR) process.

### Objectives

#### Phase I

1. Assure safety of bench scale operations.
2. Secure basic sensitivity data (initiation, transition, propagation) for pilot plant design, for engineering analysis and pilot plant Fault Tree Analysis.
3. Construct preliminary Logic Model (Fault Tree) of the pilot plant.
4. Coordinate safety data with engineering design.

#### Phase II

1. Perform a preliminary engineering analysis on equipment chosen for pilot plant operation with regard to potential hazards and safety margin.
2. Determine transition capability of the reactor mixture in a 4 inch by 12 foot reaction tube.
3. Refine logic model for simulation.

#### Phase III

1. Final engineering analysis of selected pilot plant equipment.
2. Perform a risk analysis of the pilot plant operation and conduct trade-off design modifications should an unacceptable risk be encountered.

### Summary and Conclusions

Data from sensitivity tests indicate that materials in the pilot plant process are relatively insensitive to impact, friction, ESD and thermal stimuli.

It has been determined that no material in the pilot plant equipment will transit from burning to explosion. In other words, the pilot plant system is not capable of acting as an explosive shock donor to process materials.

Two materials (reaction mixture and guanidine nitrate) will propagate an explosive reaction if sufficiently boosted. The critical diameter for each is less than one inch. Other materials in the pilot plant will not sustain an explosive reaction in the one inch interconnecting pipelines.

A detailed engineering analysis of selected pilot plant equipment for possible hazards and safety margins has shown no hazards for normal operating conditions. Abnormal occurrences; such as, metal/metal contact between impellers and pump cages or mix blades and tanks would cause initiation. However, transition data show that only a fire would result.

Computer simulation of the logic model (Fault Tree) yielded 152 potential initiation modes, 21 of which were considered to be critical or most probable of occurring. The simulation was performed over 800 hours of operation with no maintenance or repair and resulted in a probability of initiation of  $4.6 \times 10^{-3}$  or a corresponding probability of no initiation of 0.9953. This is an acceptable risk (initiation only) since the losses due to initiation during operation of the pilot plant would be minimal when compared to the cost of reducing the probability of initiation by (1) scheduled maintenance, (2) replacement of designated equipment on a regular basis, or (3) redesign of equipment. However, if the presently designed pilot plant were to be scaled up to a production plant operating over a span of years where any downtime or interruption of the process would have a significant effect on the safety, cost and productivity of the facility, a recommendation for scheduled maintenance, repair or redesign might be warranted.

## DISCUSSION

### Material Sensitivity

Initiation testing of materials was completed during Phases I and II of this contract. These tests consisted of subjecting in-process materials to impact, friction and ESD (electrostatic discharge) stimuli and obtaining threshold initiation level (TIL's) for each material. Results of the tests are summarized in Table I. An inspection of Table I shows that the materials in the BMR process and selected combinations are relatively insensitive. Many of the samples tested could not be initiated at the limits of the standard test machines and are so indicated when a greater than or equal sign ( $\geq$ ) precedes a data point. For impact, the failure to initiate a sample by dropping a 2 kg weight from a height of 120 cm (over a known impact area) is the limit of the impact machine. The energy input is calibrated periodically.

- (1) Level above which initiation can occur as a result of 20 consecutive failures at that level.

A friction TIL value was obtained for AN/GN/U = 45/40/15, all others exceeded the limits of the test. The maximum pressures tested at a given velocity (1 inch slide distance) are in Table I.

The TIL values for ESD ranged from 0.075 to 1.26 joules, a spread of only two test levels, and are considered to be high. They are above the energy region that could be available from a human being (0.013 joules max).

In all sensitivity testing, the Model 300 Lira Analyzer was used to determine if initiation occurred. The Lira is a precision instrument that analyzes selected components of a gas mixture to determine their presence and concentration. The Lira analyzes a sample gas by comparing its infrared absorption characteristics with the constant infrared absorption characteristics of a known gas. The Model 300 is modified to operate as a detector of the decomposition gases CO, CO<sub>2</sub>, NO<sub>2</sub> and NO. Therefore, initiation does not necessarily mean that a flash fire or smoke (visual indication) will result, but rather that some decomposition occurs which produces gaseous products detected by the Lira. This is a much more critical definition of initiation.

Results of the Differential Scanning Calorimeter tests are shown in Table II. Relatively high temperatures (266 to 295°C) had to be reached before any exothermic reaction occurred.

All samples (except the pure ingredients) subjected to the various initiation sources were stoichiometric mixtures (balanced to CO<sub>2</sub>, H<sub>2</sub>O, N<sub>2</sub>) that represent the "worst case" conditions that could occur in the process.

#### Transition Testing

Transition tests were performed to determine the effect of initiation on the ability of a material to transit from flame initiation to an explosive reaction in terms of material height under specific environmental conditions.

Critical height (transition) test results are shown in Table III. Tests on the reactor mixture were performed at both ABL and Kenvil. Initial tests were run in containers smaller than pilot plant reactor tubes with the intent of extrapolating data to determine if the reactors would transit to an explosion if the material was initiated. However, no reaction occurred in a 1" x 48" container. Therefore, a 2" x 12' test was performed at the Kenvil Plant in which no explosive reaction occurred. Since material height required for explosion to occur increases as the diameter increases, it was concluded from the Kenvil tests that an explosive reaction would not occur in the 4" x 12' pilot plant reactors if initiation occurred.

Transition tests were also performed on guanidine nitrate and no explosive reaction occurred in a 1" x 24" container. Again after considering pilot plant equipment dimensions, it was concluded that no transition hazard existed in pilot plant equipment handling guanidine nitrate.

#### Propagation Tests

Propagation tests determine the explosive propagation characteristics of a material in terms of material diameter when subjected to a shock stimuli. Results of these tests are shown in Table III. The results show that guanidine nitrate and the material in the reactors will propagate an explosive reaction, since many of their critical diameters are less than one inch. However, it must be remembered that the transition tests demonstrated that these materials under the pilot plant conditions, would not transit to an explosion. In other words, the pilot plant process materials are not capable of supplying a shock stimulus for propagation to occur.

Propagation tests performed on other samples show that no propagation will occur in the one inch piping used in the pilot plant.

#### Dust Explosibility

Dust explosibility tests were performed in an effort to determine the minimum concentration and minimum energy required to initiate guanidine nitrate in a dusty atmosphere. The guanidine nitrate was screened to < 53 micron and two different sources of initiation were used. Initially a continuous sparking electrode was attempted, however, no initiation of a GN/air dust cloud could be obtained. The test was rerun using fibrous nitrocellulose as an ignition source which is a more violent source of initiation than the sparking electrodes. In both cases, the guanidine nitrate dust/air mixture could not be initiated at the standard test limits of the machine (4.1 oz/ft<sup>3</sup>).

A possible explanation of this unexpected result can be obtained by an interpretation of the DSC data and applying it to a dust cloud ignition sequence. In order for a dust cloud to ignite and sustain ignition, dust particle(s) must be raised to their ignition temperature and the heat released by their ignition must be sufficient to ignite adjacent particles and thus result in a sustained reaction. From the DSC trace, GN melts in the range of 210 to 220°C while absorbing 30-35 cal/gm. An exotherm occurs in the range of 285-316°C liberating 90-120 cal/gm. (By comparison, RDX and nitroglycerin burn and liberate about 1200-1500 cal/gm at first exotherm). The amount of heat released is enough to raise the temperature an additional 100°C or to approximately 385 to 415°C. GN dust cloud ignition temperature ranges from 390°C (ABL data) to 500°C.<sup>(1)</sup> Therefore, it could be reasoned the ignition of GN dust particles does not result in the liberation of enough heat to ignite adjacent dust particles to sustain ignition in the dust cloud.



Based on the inability to ignite or sustain ignition of a GN dust cloud up to the concentration limits of test apparatus ( $4.1 \text{ oz/ft}^3$ ), it was concluded that no dust explosion hazard existed.

#### Shipping and Storage Classification Testing

Testing in accordance with TB-700-2 was conducted on guanidine nitrate by ABL. The data from these tests are shown on Table IV. The government has used a combination of these data and its own in-house data to tentatively classify guanidine nitrate (less than 25% water wet) as Class 7 for storage and as an oxidizing agent for shipping.

#### Hazard Evaluations

The engineering analysis performed on selected equipment was performed from equipment drawings, specification and maximum operating parameters furnished by Kenvil and the Research Center. Since no on-site measurements (i.e., forces, pressures, and velocities) were made, tensile strengths or yield points of materials involved<sup>(1-3)</sup> were used to obtain safety margins. In general, the safety margins found on equipment are representative of "worst case" condition, so the analysis would be conservative from a safety point of view.

In the process where equipment handles a water slurry, the analysis was based on water-free material response data, since testing was not done with water slurries. The use of water-free material values would render conservative results, since the water would most likely act as an extinguisher for any initiation. This type of an analysis, using water-free sensitivity data, would apply to start-up or shut-down modes of operation or a process "upset condition" in which a sufficient amount of water would not be present.

Some of the items in the process were not analyzed. The densitometer and evaporator had no mechanical or moving parts. The pump in the cooling system of the crystallizer was not analyzed since it will pump water containing only a small amount of ammonium nitrate (0.1% of AN). Finally, the level controllers were not analyzed, since they had low velocity movement ( $\sim 0.06 \text{ ft/sec}$ ).

A hazards evaluation was performed on pumps, mixers, reactors, valves, centrifuges, a crystallizer and a dryer in which in-process potentials and material response data (expressed in similar engineering terms) were compared to obtain quantitative safety margins for normal and abnormal conditions. As an example, a 3450 rpm centrifugal pump with a carbon/ceramic mechanical seal was selected to pump material to the crystallizer. The velocity of the rotating seal parts was calculated to be  $16.9 \text{ ft/sec}$  with a normal pressure of 30 psi (manufacturer's specification) and an abnormal pressure of  $\sim 8000 \text{ psi}$  (yield point of carbon). Figure 1 shows a friction profile of the material being pumped (less water). By a straight line extrapolation, no



positive safety margin is realized at 16.9 ft/sec. The straight line extrapolation is conservative since friction profile curves take an asymptotic form. To obtain a positive safety factor, a data point at 17 ft/sec would have to be obtained or the pump speed reduced by reducing the rpm rating. Since testing above 10 ft/sec would result in damage to the friction machine, it was recommended that a pump with a reduced rpm be used. Such a change did not adversely affect the pilot plant operation and a 1750 rpm centrifugal pump with a teflon pack gland was selected. The in-process potential for the pump was 24 psi (normal) to ~ 5,000 psi (abnormal) at a velocity of 8.6 ft/sec. By referring to Figure 1, material response at 8.6 ft/sec is ~ 43,000 psi. By comparing the in-process potential to the material response data safety margins of 8.6 to 1797 are realized.


A similar analysis has been completed on designated pilot plant equipment. A detailed discussion with summary tables of all engineering analysis has been previously reported. (4-6) In general, all normal and some abnormal operations have adequate safety margins. Abnormal occurrences such as impellers or mix blades breaking and hitting metal parts would cause initiation (no safety margin), but as discussed in the risk analysis of this report, such events have probabilities  $5 \times 10^{-4}$  to  $5 \times 10^{-5}$  of occurring over the time of pilot plant operation.

#### Logic Model (Fault Tree)

The logic model is a concise and orderly description of various combinations of events that can lead to a predefined "undesired" event. The logic model is presented in a diagram or blueprint form and results in an engineering capability to identify and evaluate the overall effect of component failure, controls or human actions on the system.

To understand and follow the logic model, a basic knowledge of the symbols used is required. A list of the symbols used and their meaning is illustrated in Table V. The use of transfer symbols (triangles) deserves some comment since they are used in two ways: (1) for transferring a section of the model that has been previously developed under identical circumstances from another section, and (2) transfer similar logic from one piece of equipment that applied to another piece of equipment. Use of transfers in this second method means that only the logic or events are the same, but probabilities of the events may be different since it is a different piece of equipment handling different materials.

The uses of transfer symbols may be best explained by using an example for each of the ways they are employed. On page A-4 of the logic model, an event for possible friction initiation "Impeller hits tank wall" is developed. Under this event a transfer symbol  is shown. On the same page for possible impact initiation, the same event in the same tank "Impeller hits tank wall" is shown. Since the event was already developed, it is transferred by use of the symbol .

On page A-8, another event "Impeller hits tank wall" is shown. The logic to develop this event is the same as that on page A-4, but applies to a different mixer. Therefore, a transfer  is used to show such a transfer. Table VI lists all transfer used and their origination point in the logic model.

#### Risk Analysis for Guanidine Nitrate Pilot Plant

The logic model constructed in support of this analysis yielded a total of 152 potential failure modes. Of these, only 21 of the modes were considered to be significant or critical. These failure modes would result in, at most, initiation and not transition to explosion.

These failure modes and their respective probabilities of occurrence are given in Table VII. The basic failure modes are impeller, shaft, and/or alignment. As noted, the probabilities of failure are not the same throughout Table VII. These differences arise from a careful engineering analysis of the potential failure modes and the utilization of known failure rates. Also, the probability is calculated such that 800 hours of continuous operation have been assumed.

The probability of initiation then becomes the product of the probability of failure, times the proportion of operating time the failure rate applies, times the material response probability. For example, the impeller, shaft and shaft packing for the Goulds Pump (mixing system) had a combined failure rate of seven per million operating hours ( $7 \cdot 10^{-6}$ ). Thus, after 800 hours, the probability of failure becomes  $7 \cdot 10^{-6}$  times 800 or  $5.6 \cdot 10^{-4}$  as given in Table VII. Multiplying this probability of  $5.6 \cdot 10^{-4}$  times the proportion of operating time it applies, times material response probability gives an overall probability of initiation, or  $5.6 \cdot 10^{-4}$  times 1.0 times 0.98 or  $5.6 \cdot 10^{-4}$  as given in the last column of Table VII. The other probabilities of Table VII were derived in a like manner. Thus, Table VII gives the probability of initiation for each failure mode plus the overall probability for the pilot plant, which is  $4.6 \times 10^{-3}$ . It must be emphasized that this probability assumed 800 hours at continuous operation without repairs or maintenance. Any such action within the 800 hours would tend to reduce this probability to a much smaller quantity.

It has been shown that no transition is possible for guanidine nitrate material. Thus, the maximum expected losses to be experienced are those related to a localized initiation.

The question immediately arises, are there cost advantages to having a preventative maintenance program to reduce the potential of initiation? The answer to the posed question lies in a trade-off study between the cost of such a program versus the expected loss should initiation occur.

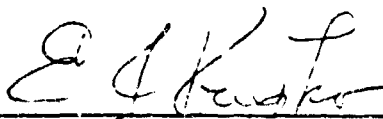
Expected Loss

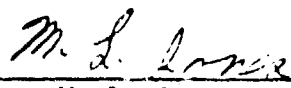
As indicated, if initiation occurs, it remains local as no transition to an explosion is possible. Thus, the expected loss becomes the product of the probability of initiation times the sum of the following cost:

- (1) Pump or equipment replacement cost.
- (2) Labor necessary to replace the pump, and clean-up from the deluge system.
- (3) Production losses while the equipment is being replaced.

For the pilot plant, a liberal estimate of total cost to be incurred, if initiation arises, is \$5,000. This times the probability of initiation anywhere in the pilot plant gives an expected loss of  $5 \cdot 10^3 \times 4.6 \cdot 10^{-3}$  or approximately \$25. It must be pointed out however, that if initiation were to occur, then the minimum loss (\$5,000) would be experienced. The "expected loss concept" is a well recognized means at normalizing cost data in a risk analysis study.

With the minimal expected loss of \$25, any preventative maintenance cost would far exceed the estimated loss. Thus, the answer to the question, is there a cost advantage to a preventative maintenance program is obviously, no. Therefore, over the operating interval of 800 hours, no preventative maintenance program is recommended or warranted. Again, this conclusion arises, primarily, from the lack of potential for transition.

  
E. J. Krupko

  
M. L. Jones

EJK:MLJ:mjs  
Attach.

TABLE I

## SUMMARY OF SENSITIVITY DATA (BMR PROCESS)

| Sample<br>(% by wt.)    | Temperature | Threshold Initiation Level**        |                          |                 | Materials                  |
|-------------------------|-------------|-------------------------------------|--------------------------|-----------------|----------------------------|
|                         |             | Impact<br>(ft-lbs/in <sup>2</sup> ) | Friction<br>(psi/ft/sec) | ESD<br>(Joules) |                            |
| AN/U<br>1/1             | Ambient     | --                                  | ≥ 69,000/8               |                 | Steel/Steel                |
| AN/U<br>2/1             | Ambient     | --                                  | ≥ 69,000/8               |                 | Steel/Steel                |
| AN/U<br>4/1             | Ambient     | ≥ 59.7                              | ≥ 67,000/8               | 0.5             | Steel/Steel                |
| AN/U<br>4/1             | 135°C       | $84 \times 10^3$ *                  | ≥ 39,090/8               |                 | Steel/Steel                |
| AN/CN/U<br>45/40/15     | 60°C        | > 77.6                              | 45,614/8<br>35,185/10    |                 | Steel/Steel<br>Steel/Steel |
| AN/CN/U<br>67/24/9      | 130°C       |                                     | ≥ 58,870/10              |                 | Steel/Steel                |
| CN - Pure               | Ambient     | ≥ 59.7                              | ≥ 122,400/8              | 1.26            | Steel/Steel                |
| CN - Technical<br>Grade | Ambient     | 31.6                                | > 105,800/8              | 0.075           | Steel/Steel                |

\* ft-lbs/sec

\*\* Level above which initiation can occur as a result of 20 consecutive failures at that level.

TABLE II  
DIFFERENTIAL SCANNING CALORIMETER (DSC) TEST RESULTS

AN/U  
1/1

Heating Rate  
(°C/min)

20  
40  
80

Endotherm at 240°C

--  
--

AN/U/Sil Gel  
2/2/1.7

Heating Rate  
(°C/min)

20  
40  
80

Exotherm Began

266°C  
276°C  
295°C

Peak Value

280°C  
290°C  
320°C

GN

Heating Rate  
(°C/min)

5  
10  
20

Exotherm Began

--  
285°C  
292°C

Peak Value

--  
307°C  
316°C

TABLE III  
EXPLOSIVE CHARACTERISTICS OF MATERIALS

| <u>Sample</u>            | <u>Dust Explosibility</u> | <u>Critical Height</u>          | <u>Critical Diameter</u>                            |
|--------------------------|---------------------------|---------------------------------|---|
| GN                       | ≥ 4.1 oz/ft <sup>3</sup>  | ≥ 24" for a 1" diameter pipe    | < 1" 1" dia - 2980 m/sec<br>2 1/2" dia - 3980 m/sec |
| Reactor Mixture (200°C)  |                           | ≥ 48" for a 1"(1) diameter pipe | < 1"  |
| Reactor Mixture (200°C)  |                           | ≥ 12' for a 2"(2) diameter pipe |   |
| 34/38/28 GN/AN/U at 60°C |                           |                                 | > 1"  |
| AN/U at 100°C<br>4/1     |                           |                                 | > 1"  |

Propagation Test for GN in a Tray (6" deep x 12" wide x 24" long)

- 1" Booster - no propagation
- 2" Booster - propagation - 2900 m/sec

- (1) Performed at ABL
- (2) Performed at Kenvil Plant

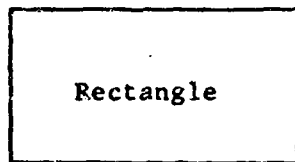
TABLE IV  
HAZARD CLASSIFICATION TESTS  
FOR GUANIDINE NITRATE  
BY  
TB 700-2 CRITERIA

| <u>Test</u>                             | <u>Result</u>                                     |
|---|---|
| Detonation Test<br>(No. 8 Blasting Cap) | No deformation of pressure plate<br>or cylinder   |
| Ignition and Unconfined<br>Burning Test | Burning reaction only                             |
| Thermal Stability Test                  | No color or visible change in<br>48 hours at 75°C |
| Card Gap Test                           | Failure at zero cards                             |
| Impact Sensitivity Test                 | No ignition at 47.3 inches (120 cm)               |



TABLE V  
GLOSSARY OF SYMBOLS COMMONLY EMPLOYED  
ON FAULT TREE DRAWINGS

Event Representation



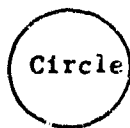
The rectangle identifies an event that results from the combination of fault or hazard events through the input logic gate.



The diamond describes a fault or hazard that is basic in a given fault tree, but undeveloped at this level. The reasons for it being undeveloped are, necessary information not available, insufficient consequence or limited scope of analysis.



The house indicates an event that is normally expected to occur.



The circle describes a basic fault event that requires no further development.

Logic Operations

Output



Inputs

"And Gate" describes the logical operation whereby the coexistence of all input events is required to produce the output event.

TABLE V (CONTINUED)

Output

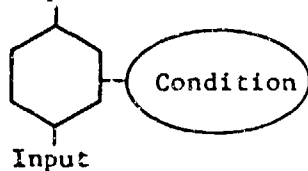


Input

"Or Gate" defines the situation whereby the output event will exist if one or more of the input events exist.

Output

Inhibit Gate



Input

Inhibit gates describe a casual relationship between one fault and another. The input event directly produces the output event if the indicated condition is satisfied.

Triangles



The triangles are used as transfer symbols. A line from the apex of the triangle indicates a "transfer in" and a line from the side denotes a "transfer out."



Similarity transfer denotes the transfer of logic only from another part of the tree.

TABLE VI

## ORIGINATION POINT FOR TRANSFER SYMBOLS IN THE LOGIC MODEL

| <u>Transfer</u> | <u>Origination<br/>(page)</u> | <u>Transfer</u> | <u>Origination<br/>(page)</u> |
|-----------------|-------------------------------|-----------------|-------------------------------|
| 1A              | A-2                           | 4F              | A-10                          |
| 1B              | A-2                           | 4G              | A-9                           |
| 1C              | A-2                           | 5A              | A-11                          |
| 1D              | A-2                           | 5C              | A-11                          |
| 2A              | A-4                           | 5D              | A-11                          |
| 2B              | A-4                           | 5E              | A-11                          |
| 2C              | A-4                           | 5F              | A-12                          |
| 2D              | A-5                           | 6A              | A-13                          |
| 2F              | A-5                           | 6B              | A-14                          |
| 2G              | A-5                           | 6C              | A-15                          |
| 2H              | A-3                           | 6D              | A-15                          |
| 2J              | A-3                           | 6E              | A-13                          |
| 2K              | A-3                           | 6F              | A-15                          |
| 2L              | A-3                           | 7A              | A-16                          |
| 2M              | A-3                           | 7B              | A-16                          |
| 3A              | A-6                           | 7C              | A-17                          |
| 3B              | A-7                           | 7D              | A-17                          |
| 3C              | A-7                           | 7E              | A-18                          |
| 3D              | A-6                           | 7F              | A-18                          |
| 3E              | A-6                           | 7G              | A-17                          |
| 3F              | A-7                           | 7H              | A-18                          |
| 3H              | A-7                           | 8A              | A-20                          |
| 3J              | A-7                           | 8B              | A-20                          |
| 3K              | A-7                           | 8C              | A-20                          |
| 4A              | A-9                           | 8D              | A-20                          |
| 4B              | A-8                           | 9A              | A-19                          |
| 4C              | A-10                          | 9B              | A-19                          |
| 4D              | A-10                          | 9C              | A-19                          |
| 4E              | A-10                          |                 |                               |

TABLE VII. PROBABILITIES OF FAILURE SUMMARY FOR CRITICAL FAILURE MODES

| Item  | Failure   | Type of Hazard  | Failure Probability (1)                      | Proportion of Time Failure Applies (2) | Material Response Probability      | Probability of Initiation                    |
|---|---|-----------------|--|--|------------------------------------|--|
| Mixer (Mixing System)   | Impeller, Shaft                                 | Impact Friction | $5.6 \times 10^{-5}$<br>$5.6 \times 10^{-5}$ | 1.0<br>1.0                             | 0.98<br>0.98                       | $5.5 \times 10^{-5}$<br>$5.5 \times 10^{-5}$ |
| Goulds Pump (Mixing System)   | Impeller, Shaft, or Shaft Packing               | Impact Friction | $5.6 \times 10^{-4}$<br>$5.6 \times 10^{-4}$ | 1.0<br>1.0                             | 0.98<br>0.98                       | $5.5 \times 10^{-4}$<br>$5.5 \times 10^{-4}$ |
| Goulds Pump (Reaction System)                                       | Impeller, Shaft or Shaft Packing                | Impact Friction | $5.6 \times 10^{-4}$<br>$5.6 \times 10^{-4}$ | 1.0<br>1.0                             | 0.98<br>0.98                       | $5.5 \times 10^{-4}$<br>$5.5 \times 10^{-4}$ |
| Mixer (Aqueous Quench)  | Impeller or Shaft                               | Impact Friction | $5.6 \times 10^{-5}$<br>$5.6 \times 10^{-5}$ | 1.0<br>1.0                             | 0.98<br>0.98                       | $5.5 \times 10^{-5}$<br>$5.5 \times 10^{-5}$ |
| Goulds Pump (Aqueous Quench)  | Impeller, Shaft or Shaft Packing                | Impact Friction | $5.6 \times 10^{-4}$<br>$5.6 \times 10^{-4}$ | 1.0<br>1.0                             | 0.98<br>0.98                       | $5.5 \times 10^{-4}$<br>$5.5 \times 10^{-4}$ |
| Mixer (Crystallizer System)   | Impeller or Shaft                               | Impact Friction | $5.6 \times 10^{-5}$<br>$5.6 \times 10^{-5}$ | 0.5<br>0.5                             | 0.98<br>0.98                       | $2.7 \times 10^{-5}$<br>$2.7 \times 10^{-5}$ |
| Goulds Pump (Crystallizer System)                                   | Impeller, Shaft or Shaft Packing                | Impact Friction | $5.6 \times 10^{-4}$<br>$5.6 \times 10^{-4}$ | 0.5<br>0.5                             | 0.98<br>0.98                       | $2.7 \times 10^{-4}$<br>$2.7 \times 10^{-4}$ |
| Crystallizer (Crystallizer System)                                  | Impeller, Shaft, Bearings or Improper Alignment | Impact Friction | $1.9 \times 10^{-4}$<br>$1.9 \times 10^{-4}$ | 0.5<br>0.5                             | 0.98<br>0.98                       | $9.3 \times 10^{-5}$<br>$9.3 \times 10^{-5}$ |
| Goulds Pump (Centrifuge System)                                     | Impeller, Shaft or Shaft Packing                | Impact Friction | $5.6 \times 10^{-4}$<br>$5.6 \times 10^{-4}$ | 0.125<br>0.125                         | 0.98<br>0.98                       | $6.8 \times 10^{-5}$<br>$6.8 \times 10^{-5}$ |
| Dryer   | Paddle, Shaft or Shaft Bearings                 | Impact          | $1.3 \times 10^{-4}$                         | 1.0                                    | 0.7                                | $9.1 \times 10^{-5}$                         |
| Goulds Pump (Evaporation)   | Impeller, Shaft or Shaft Packing                | Impact Friction | $5.6 \times 10^{-4}$<br>$5.6 \times 10^{-4}$ | 0.1<br>0.1                             | 0.98<br>0.98                       | $5.5 \times 10^{-5}$<br>$5.5 \times 10^{-5}$ |
| (1) Failure rate times 800 hours.                                   |   |                 |  |  | (System) Probability of Initiation |  |
| (2) Proportion of hours out of 800 the equipment will be operating. |   |                 |  |  | (System) Reliability               |  |
|   |   |                 |  |  | 46.4 x 10 <sup>-4</sup><br>0.99536 |  |

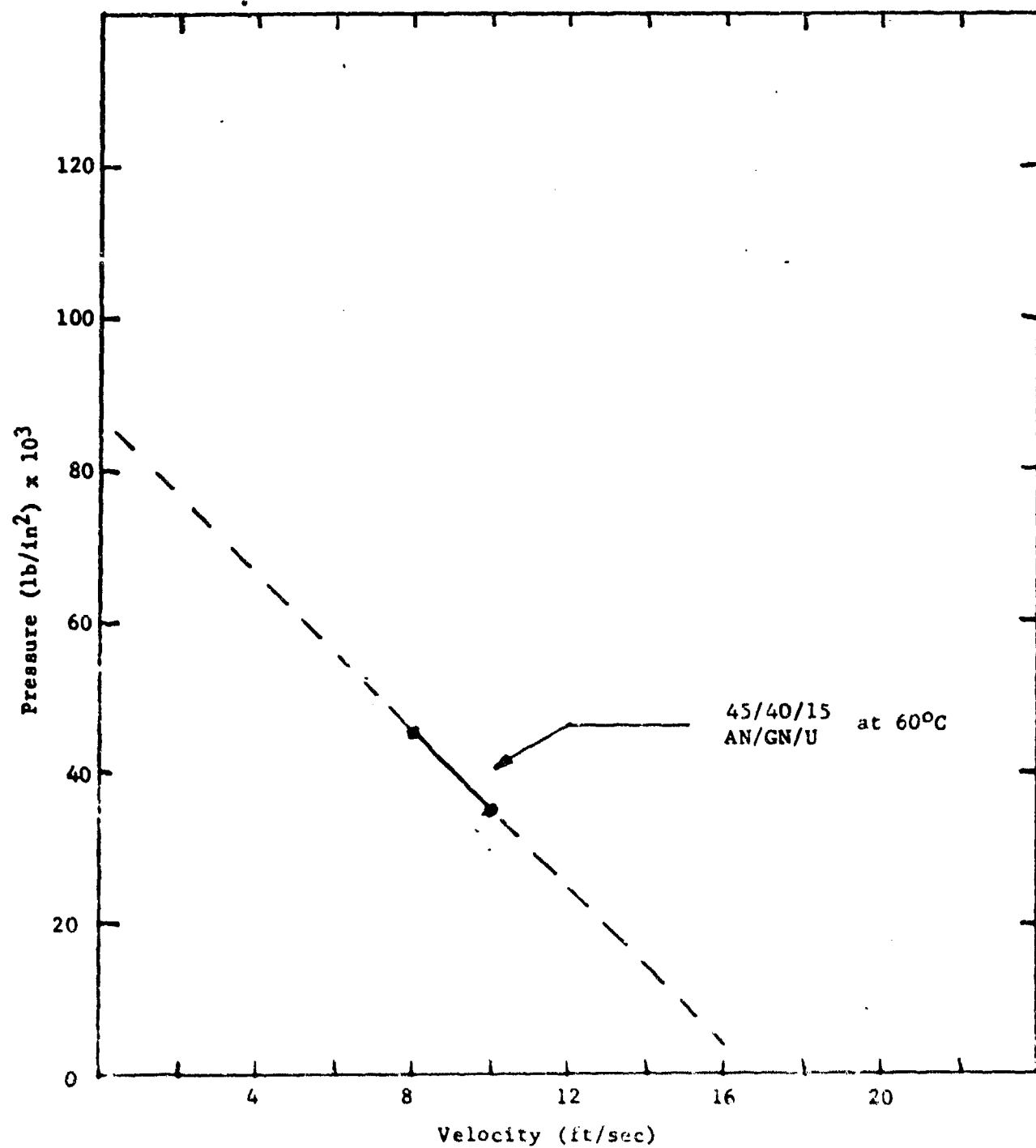
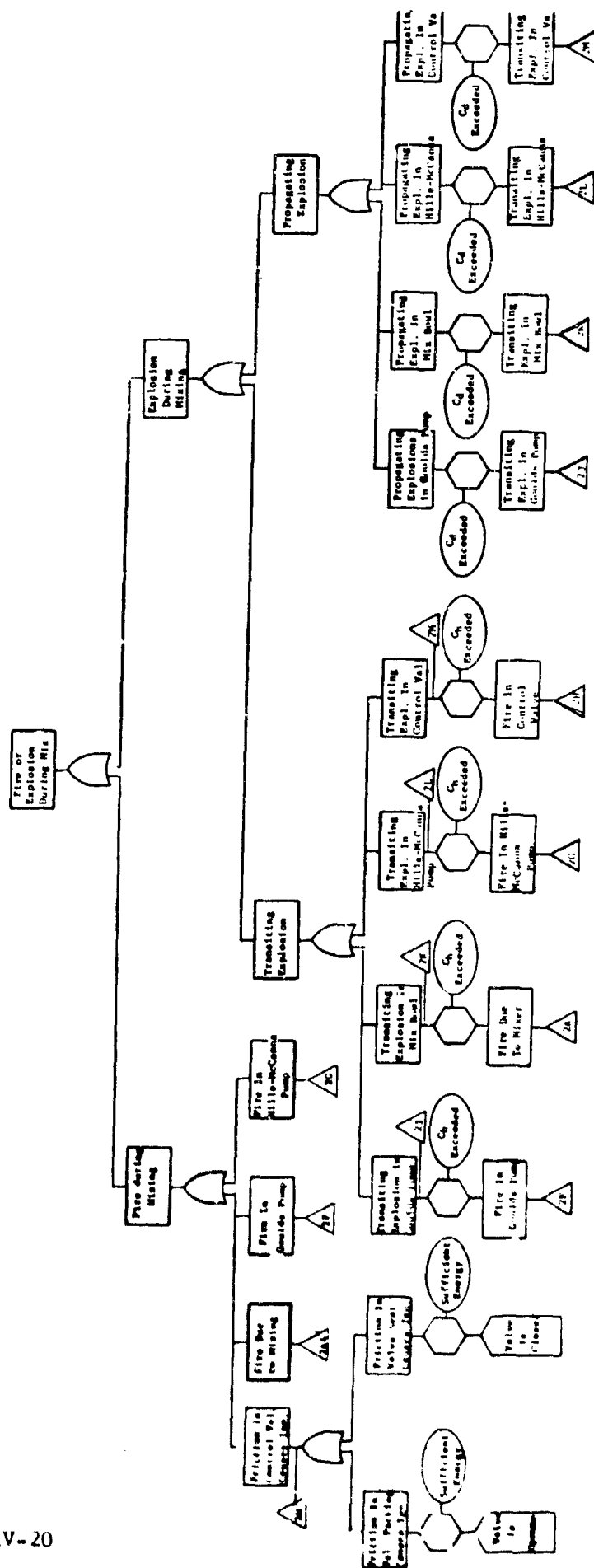


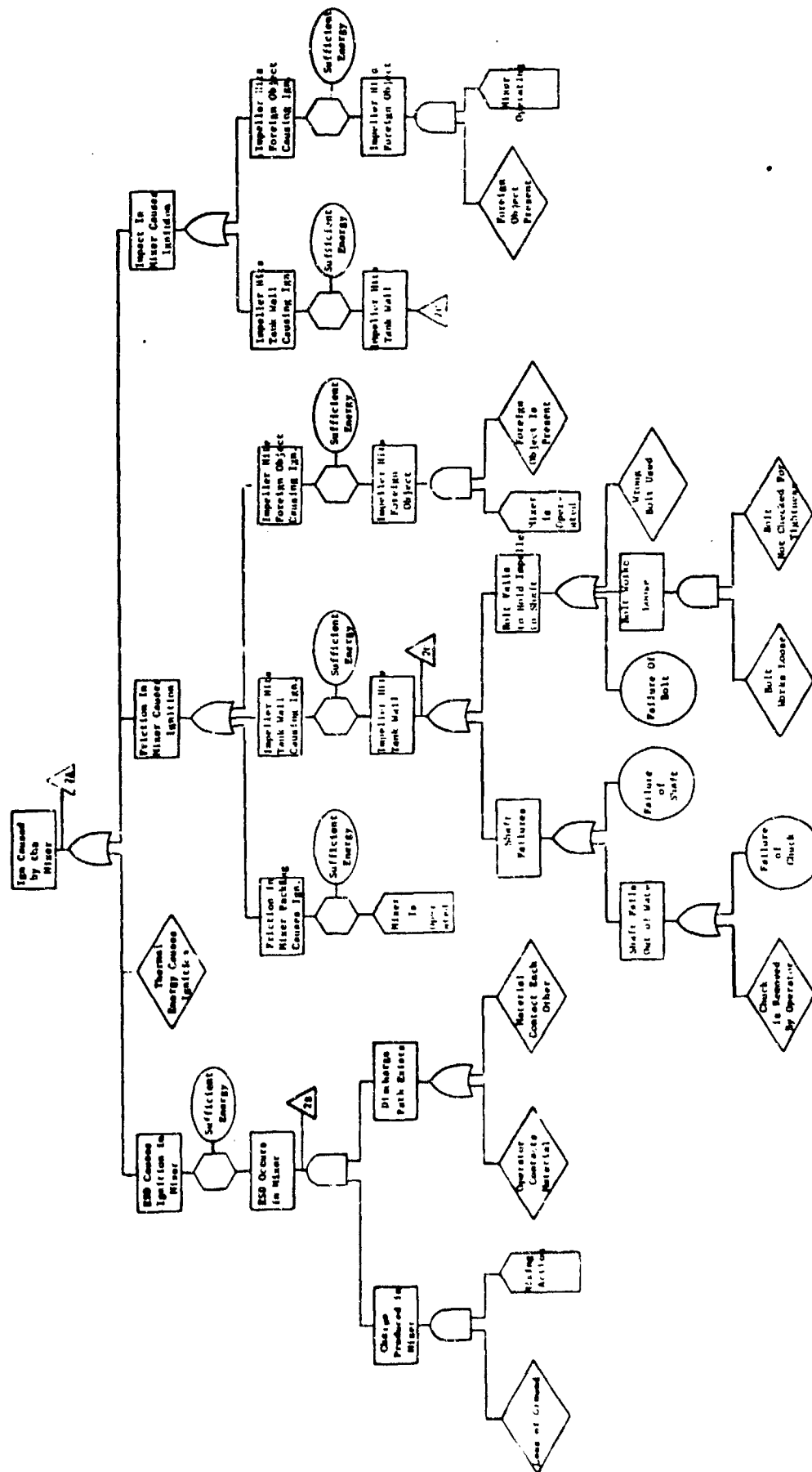
Figure 1. Friction Profile (Pressure vs. Velocity)

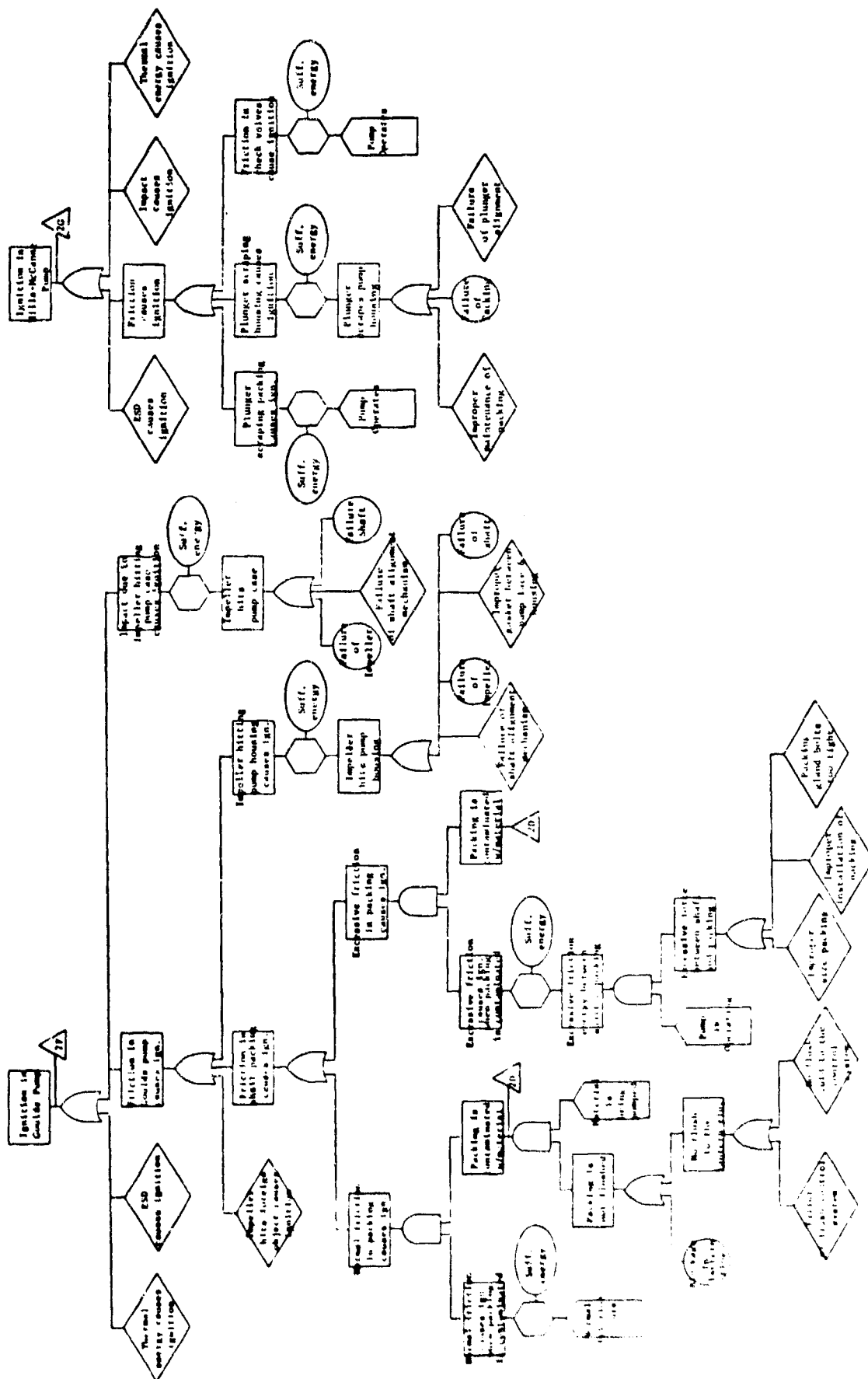






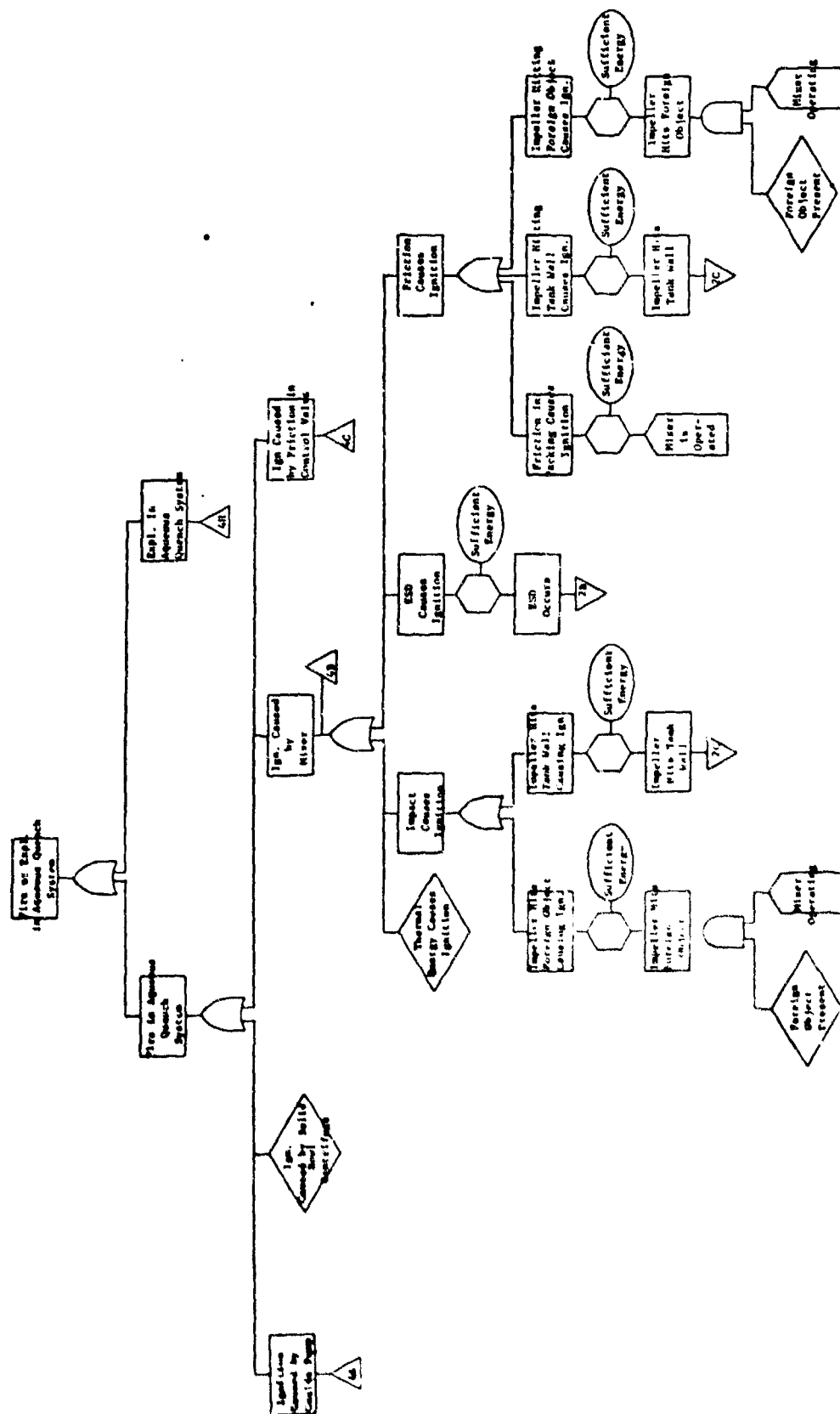


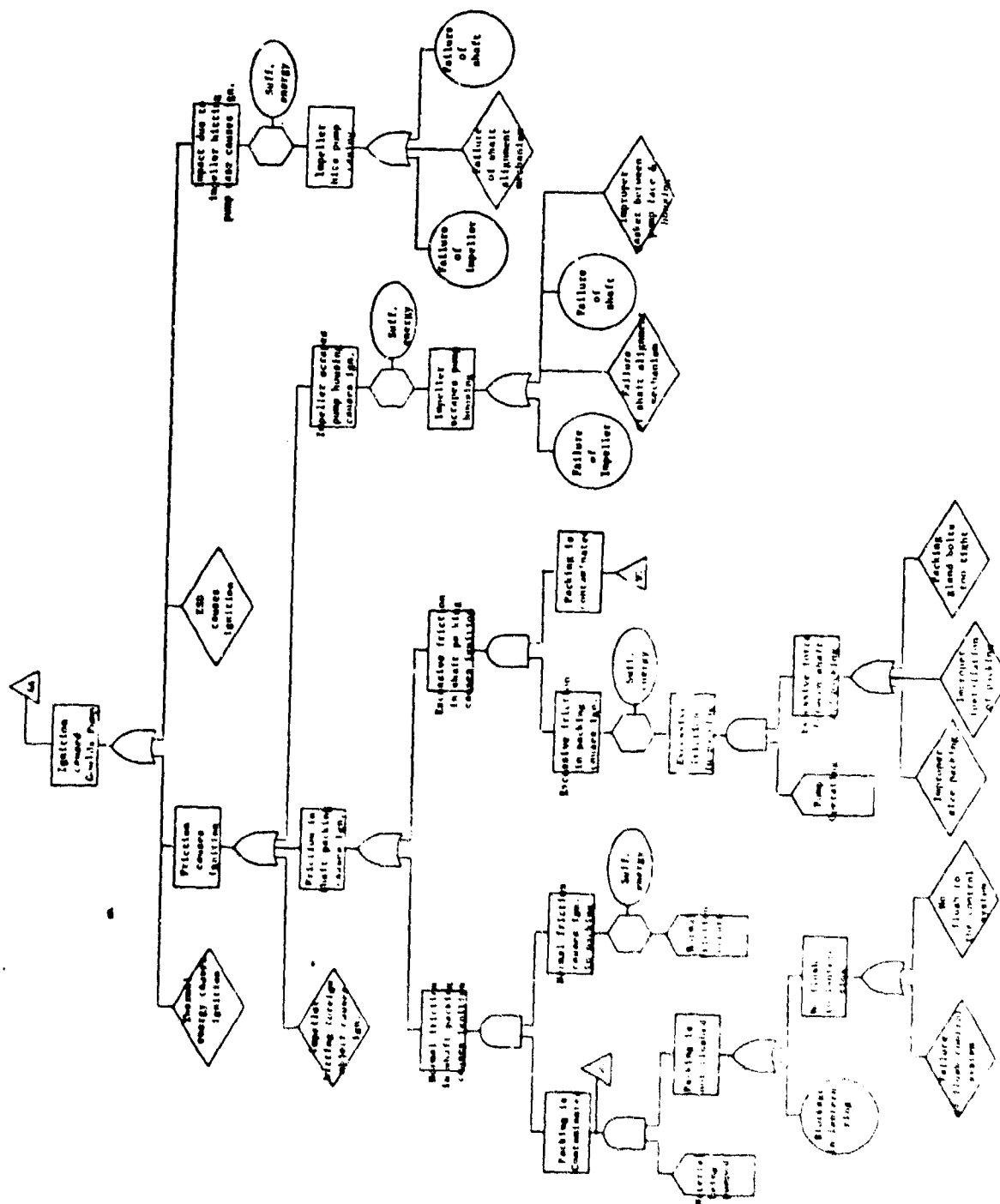


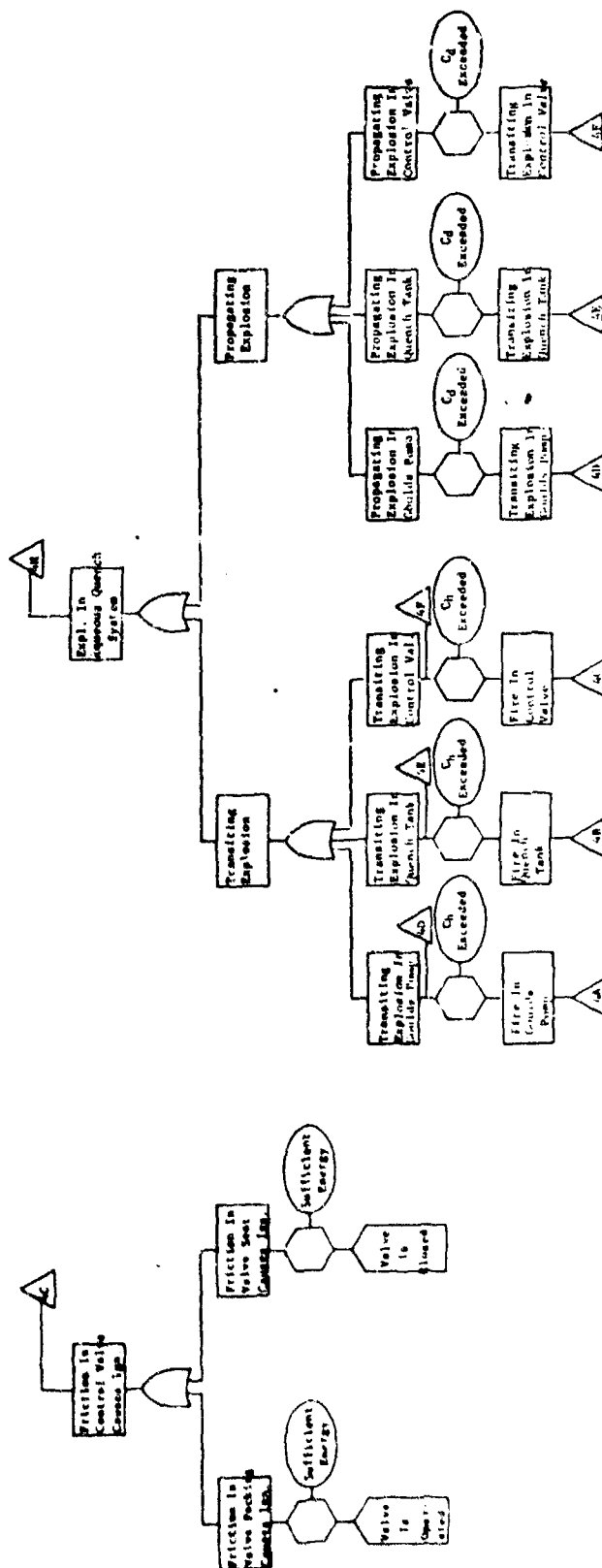


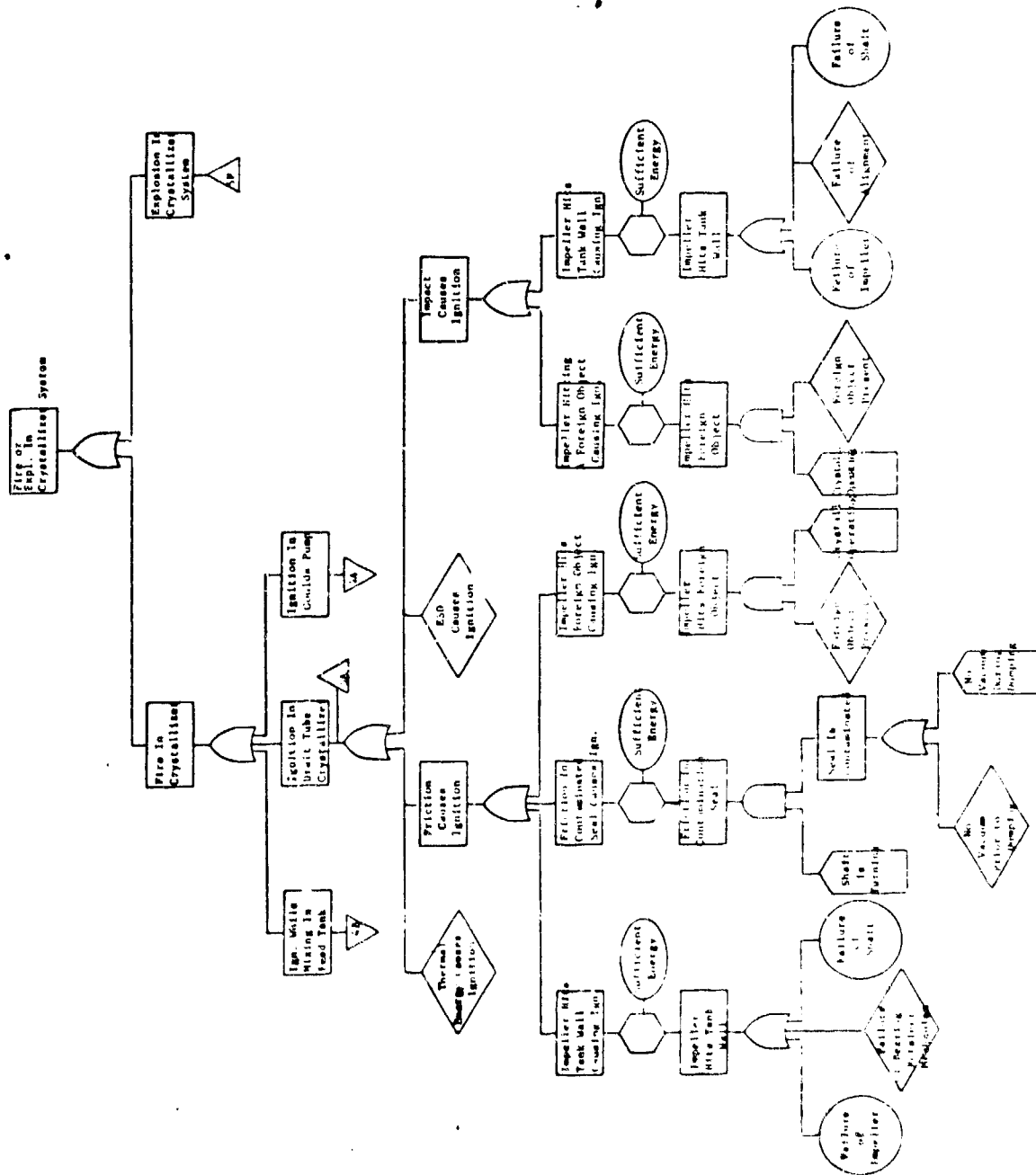




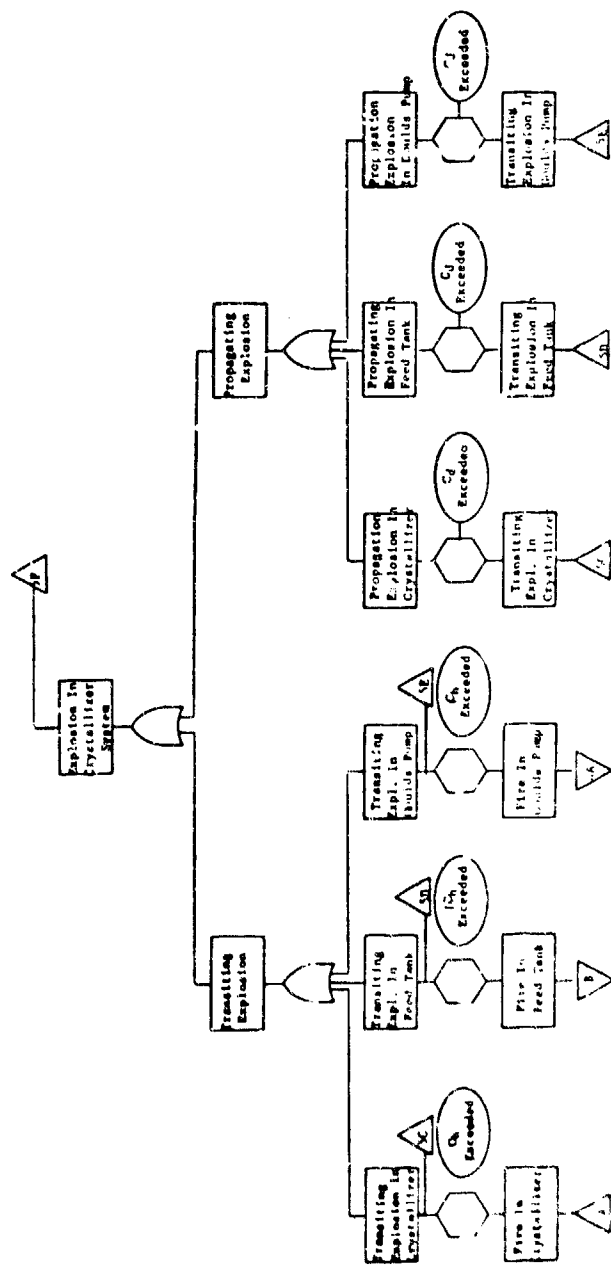


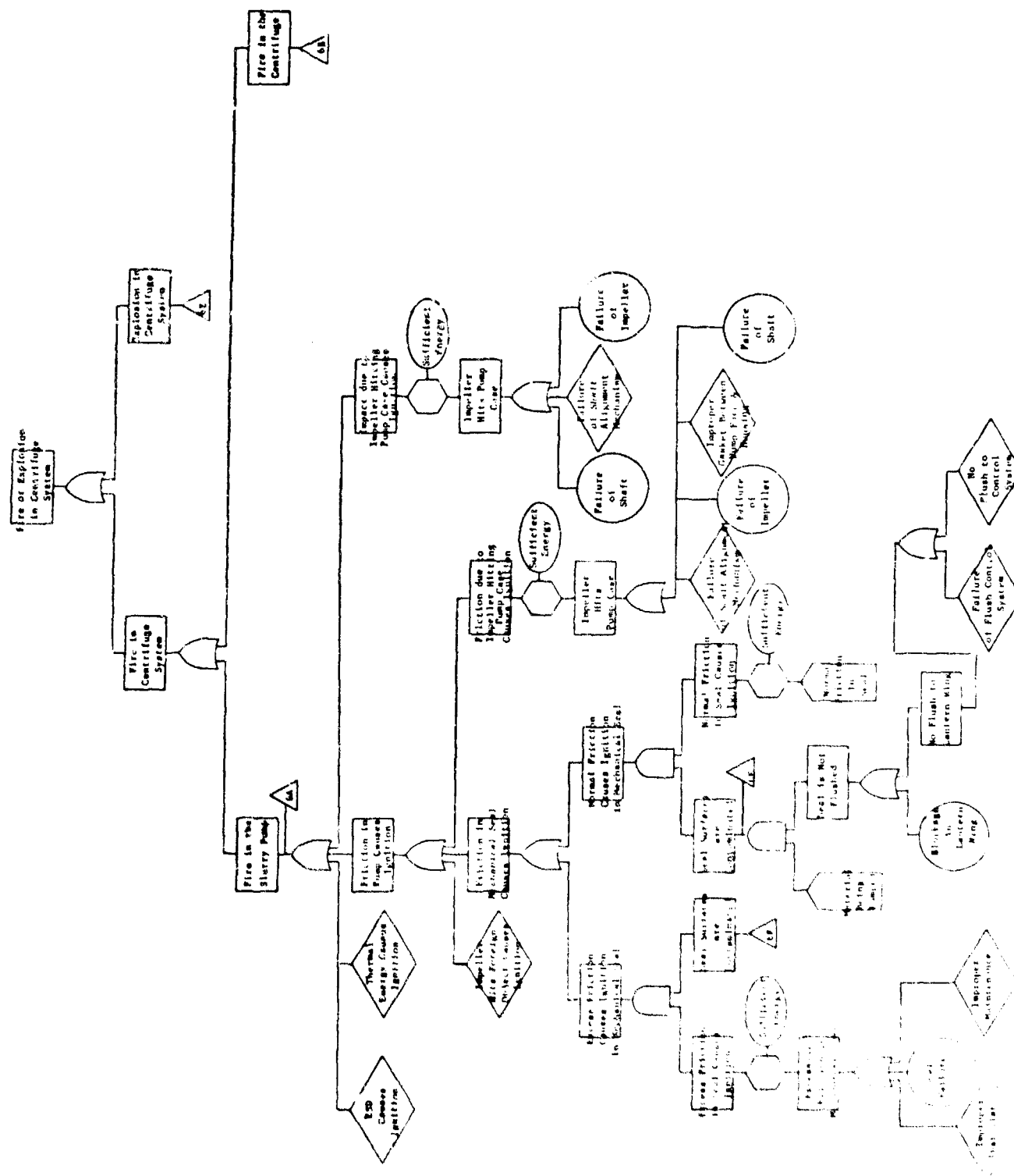


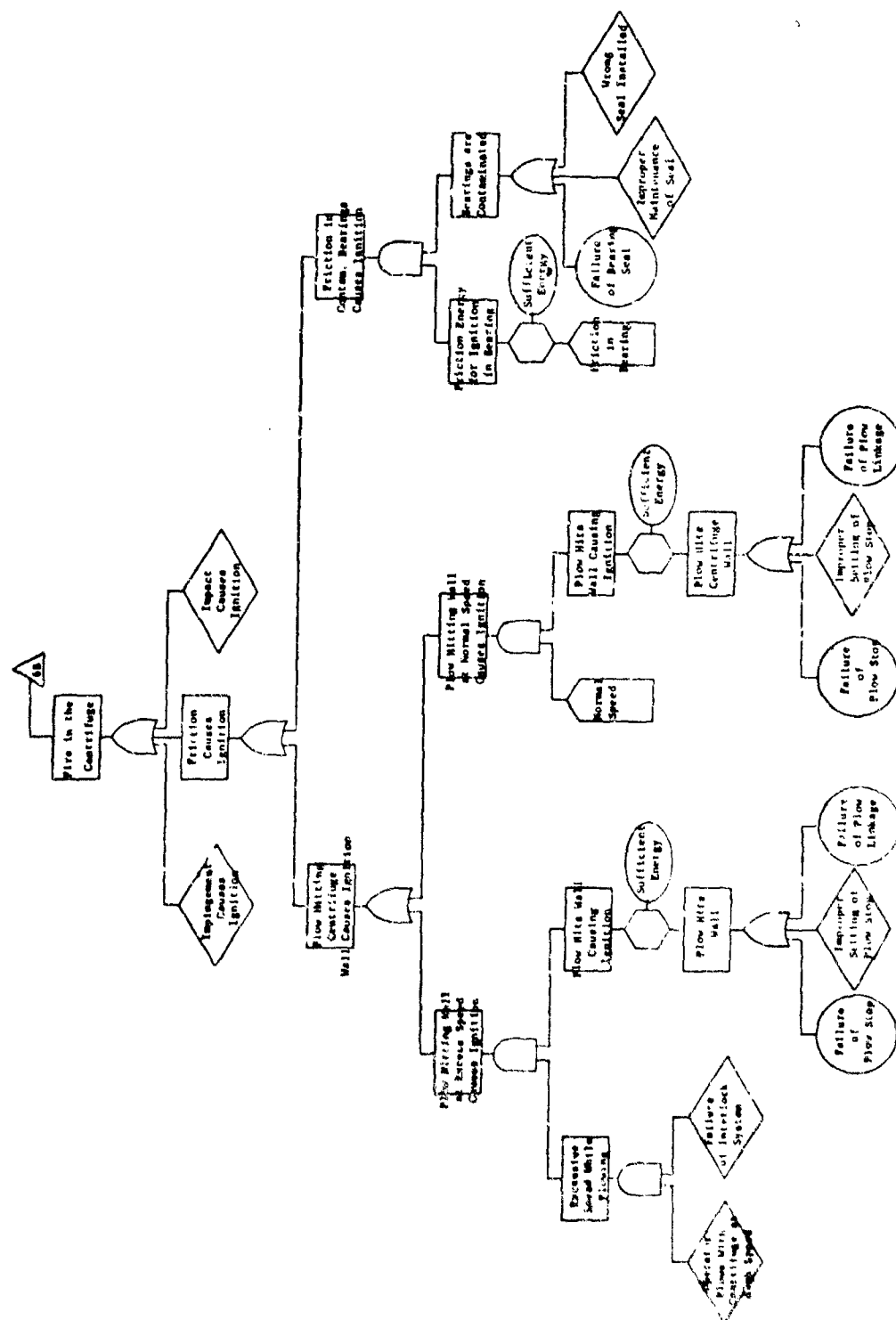


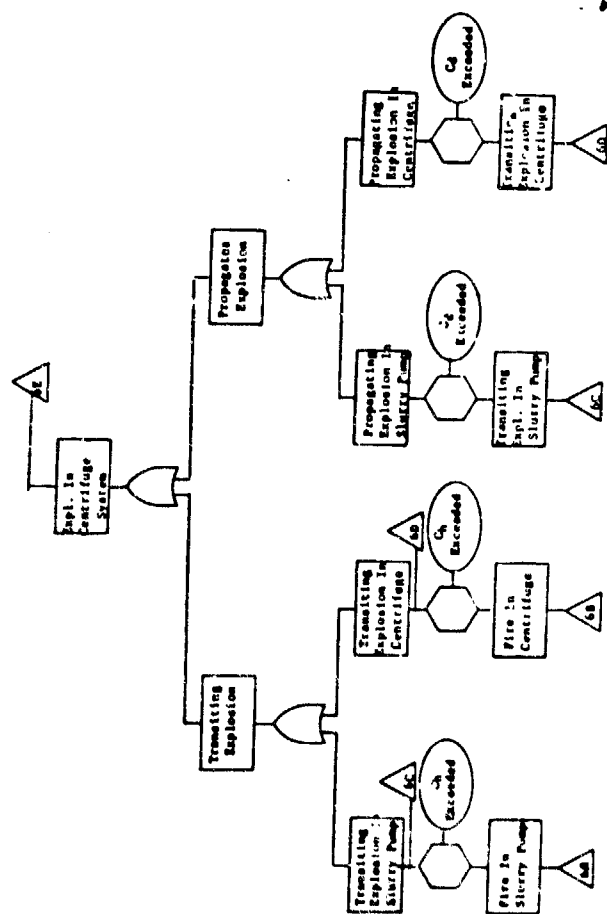


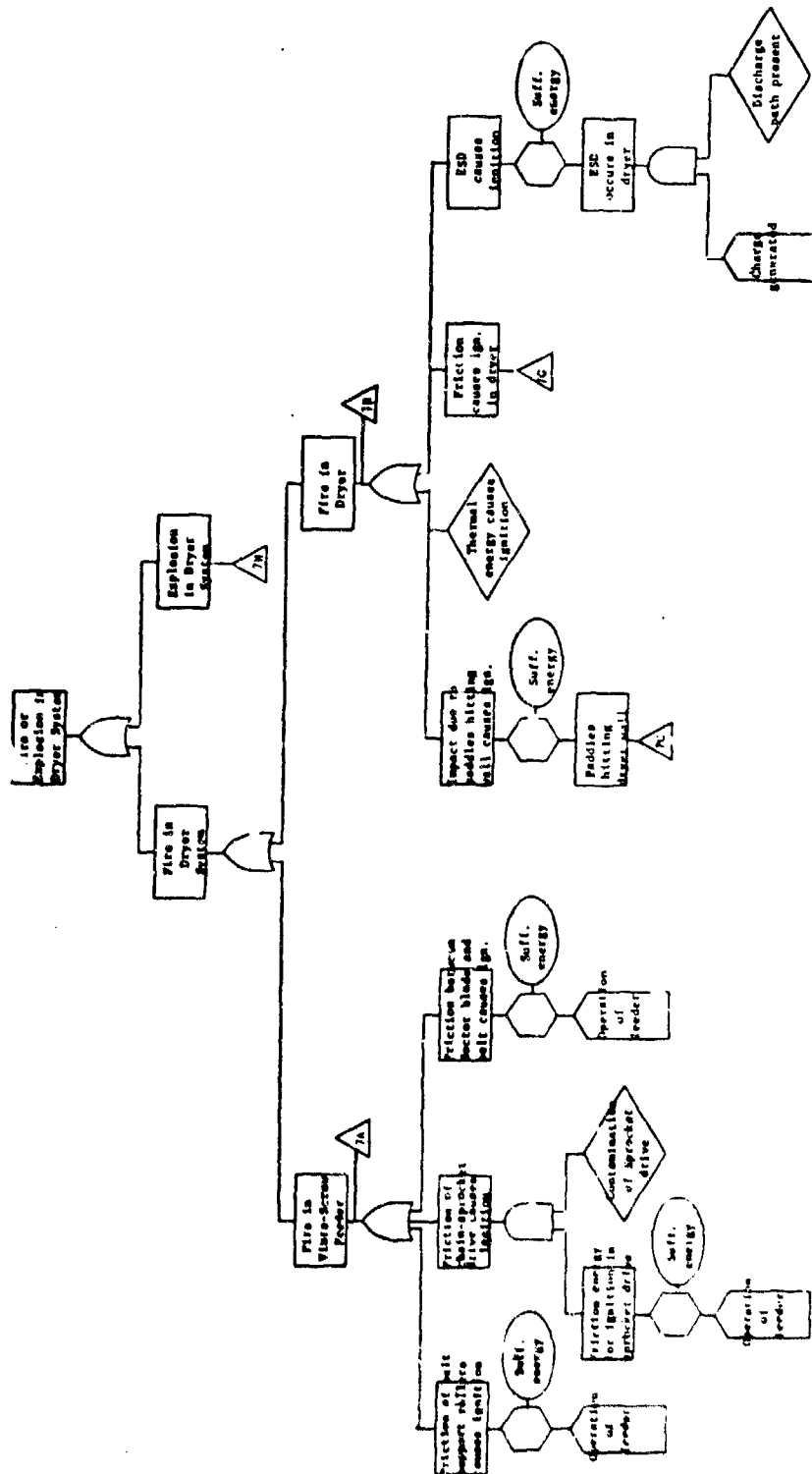






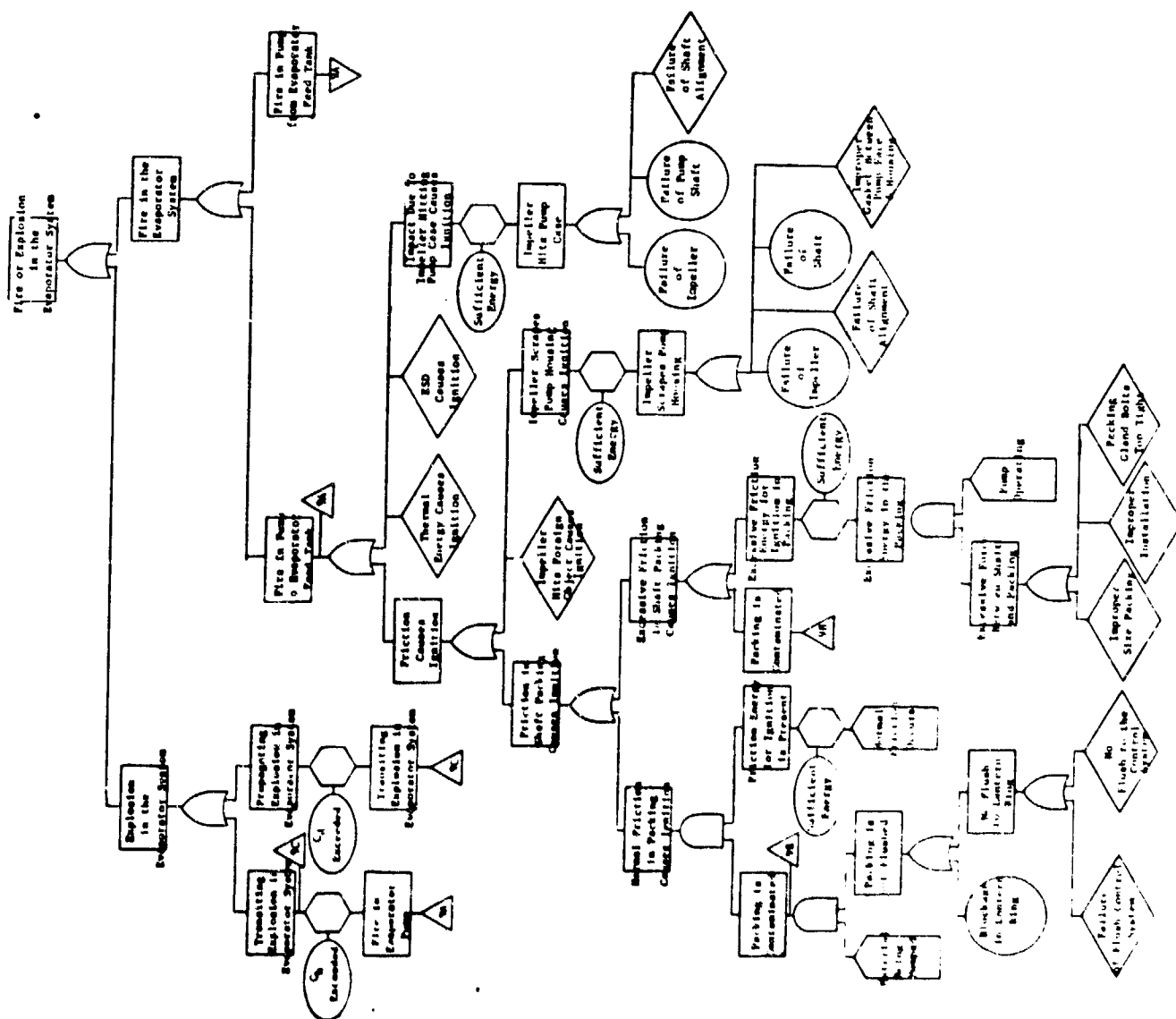
















APPENDIX V

LITERATURE SEARCH - RELATED TO PRODUCTION OF  
GUANIDINE NITRATE FROM UREA

## APPENDIX V

### LITERATURE SEARCH

#### RELATED TO PRODUCTION OF GUANIDINE NITRATE FROM UREA

by John T. Hays  
Hercules Research Center

#### Introduction

Work in progress at Hercules Kenvil Plant and the Research Center on production of guanidine nitrate from urea led to a request for a literature search on this general subject. The objectives of this search were: to make certain that recent literature on the basic process has been covered, and to develop information relative to production of by-products and their possible effects on catalyst performance. Chemical Abstracts was thoroughly checked from 1956 through October 16, 1972 and in some areas from 1947. The information is divided into four general categories: (1) Production of guanidine nitrate from urea. (2) Reactions of urea at temperatures from 100°C. to 200°C. This subject is of interest in connection with formation of by-products in the urea-ammonium nitrate feed, which is held at about 110°C. for extended periods, and in connection with formation of by-products under the reaction conditions for production of guanidine nitrate. (3) Formation of melamine from urea. This subject is of interest because it has been an active area of research in recent years and because it represents an extension of the type of catalytic reaction involved in production of guanidine nitrate. (4) Silica-phosphate reactions. This subject is of interest because of the indications from Hercules work that the diammonium phosphate used commercially to stabilize prilled ammonium nitrate decreases the activity of the silica gel catalyst used in production of guanidine nitrate from urea.

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. . . . .

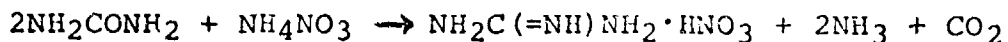
## I. Guanidine Nitrate from Urea

Little information was located in this search which was not already available to those working on the Hercules study of preparation of guanidine nitrate from urea. Nevertheless it seems worthwhile to consider the available information to get an understanding of the factors affecting the reaction.

One of the best sources of information is a report forwarded to us through the British Embassy and Picatinny Arsenal written by F. Armstrong and R. T. M. Fraser<sup>1</sup>. This report not only gives new experimental work but also gives a list of 40 references.

### A. Reaction Characteristics

Guanidine nitrate is formed from urea and ammonium nitrate by an unusual reaction:



The reaction occurs over a specific temperature range given as 175-225°C.<sup>2</sup>, with 190-200°C. preferred<sup>3</sup>, and as 160-200°C. with 180°C. giving best yields but at less than maximum rates<sup>4</sup>. Similar information is given by Russian workers<sup>5</sup>. A catalyst is required, with silica gel being preferred, although broad classes of related silica or oxide catalysts are also claimed<sup>3-5</sup>. Small scale batch reactions indicate an optimum ratio for urea:ammonium nitrate:silica gel of 1:1:1<sup>3</sup> or 2:2:1<sup>1</sup>.

The importance of the catalyst is seen when it is realized that uncatalyzed thermal decomposition of urea gives biuret and triuret at 120-160°C.<sup>6-9,13</sup>. At higher temperatures, up to 200°, cyanuric acid is formed in increasing quantities<sup>10-12,14</sup>. Heating biuret and triuret in the presence of ammonium nitrate but with no catalyst gave cyanuric acid<sup>15</sup>. With silica gel, ammonium nitrate, and urea at 195°C., the main product reported was guanidine nitrate along with 5-12% ammelide and some melamine<sup>15</sup>. Biuret and triuret are also converted to guanidine nitrate on heating with silica gel and ammonium nitrate<sup>3,15</sup>. There are thus two types of urea decomposition controlled by temperature and the presence of catalyst:

Thermal which gives mainly cyanuric acid at temperatures of 160-200°. Biuret is the main product at lower temperatures (120-160°), but its formation is reversible<sup>6,17</sup>. Ammelide and ammeline are formed in the thermal reaction but at much higher temperatures (>250°C.)<sup>19,20</sup>.

Catalytic, with silica gel and ammonium nitrate, at 180-200°C., gives mainly guanidine nitrate with small amounts of the triazine by-products, cyanuric acid, ammelide, ammeline, and melamine. Intermediate biuret and triuret are largely broken down under these conditions.

The action of the silica gel catalyst has thus led to formation of guanidine nitrate and small amounts of triazine by-products at temperatures which give cyanuric acid as the main product in the straight thermal reaction.

#### B. Reaction Mechanism

The first step in the thermal decomposition of urea is generally considered to be<sup>21</sup>:



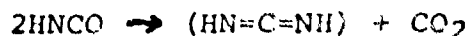
This is more than a hypothetical picture of the reaction, as proved by isolation of the HNCO product<sup>21-24</sup>, direct conversion of urea to alkali cyanates<sup>25-27</sup>, and trimerization of HNCO from urea to cyanuric acid<sup>10-12</sup>. Formation of HNCO allows ready formation of the products of the thermal decomposition of urea, i.e., formation of biuret and triuret by reaction of HNCO with urea and with biuret and trimerization of HNCO.

The products of the catalytic reaction require some other mechanism. One attractive scheme is dehydration of urea to form cyanamide<sup>5, 17, 18</sup>, known to form guanidine derivatives readily:



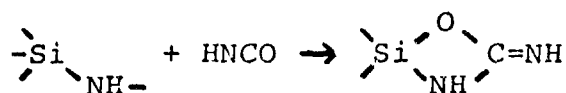
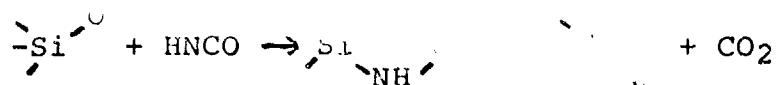
Interaction of  $\text{NH}_2\text{CN}$  and HNCO would give ammelide and ammeline<sup>17, 18</sup>, and cyanamide is also known to give melamine<sup>3</sup>.

Differential thermal analysis (DTA) data were interpreted to show the presence of cyanamide in urea pyrolysis products<sup>28</sup>, but more recent pyrolysis work has led to the conclusion that cyanamide is not a primary product of urea pyrolysis<sup>29</sup>. Infrared work has also led to the conclusion that formation of cyanamide is improbable<sup>30</sup>. Mackay<sup>3</sup> has stated that dehydration of urea does not occur, on the basis that carbon dioxide would have no effect if dehydration were the key reaction in formation of guanidine nitrate from urea and ammonium nitrate. Actually, he found that it was important to avoid  $\text{CO}_2$  build-up, which led him to postulate a splitting off of  $\text{CO}_2$ . Schmidt<sup>31</sup>, considering the analogous formation of melamine from urea, formulates it as a disproportionation of HNCO into  $\text{CO}_2$  and carbodiimide,  $\text{C}(\text{=NH})_2$ :

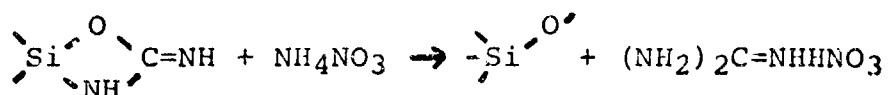


This would fit the observed effect of  $\text{CO}_2$  and the unstable intermediate would give melamine on trimerization.

Schmidt<sup>31</sup> formulates the reaction in the fashion:



Reaction of the complex with  $\text{NH}_4\text{NO}_3$  could then give guanidine nitrate.



The formation of guanidine nitrate would thus depend on reaction of ammonium nitrate with a catalyst complex. Molecular size of the ammonium salt reactant might be important in reaction with a complex with a specific steric arrangement. Kazarnovskii and Spasskaya<sup>5</sup> state that  $\text{NH}_4\text{Cl}$  and  $\text{NH}_4\text{Br}$  also form guanidine salts in this reaction but that ammonium phosphates, sulfate, carbonate, tungstate, vanadate, and salts of organic acids do not form guanidine salts in the presence of silica gel without excess pressure. The type of catalyst complex postulated could allow rationalization of this observation. The Boatright-Mackay patent<sup>2</sup> claims ammonium salts broadly, however.

It was also reported<sup>5</sup> that where best yields of guanidine were obtained with a 1:1:1 ratio of urea: $\text{NH}_4\text{NO}_3$ :silica gel, decrease of silica gel to less than 0.8 led to formation of cyanuric acid along with guanidine salt. Thus it seems necessary to provide sufficient active catalyst sites to complex the HNCO in order to avoid the "thermal" trimerization to cyanuric acid. Blocking of active -OH groups by esterification completely deactivated the catalyst<sup>1</sup>. Formation of -OR groups on silica gel by this method has been reported in detail<sup>32</sup>. Decreasing the ammonium nitrate to stoichiometric proportions also decreases yield<sup>5</sup> as might be expected on the assumption that dissociation of the catalyst-HNCO complex must be avoided.

Experiments<sup>1</sup> with  $^{15}\text{NH}_4\text{NO}_3$  and  $(\text{NH}_2)_2\text{C}=\text{O}^{18}$  showed considerable  $^{15}\text{N}$  in the ammonium carbamate recovered but less  $^{18}\text{O}$  than would be expected if all the  $\text{CO}_2$  were derived from urea. The  $^{15}\text{N}$  result suggests that the reaction:  $\text{NH}_3 + ^{15}\text{NH}_4\text{NO}_3 \rightarrow ^{15}\text{NH}_3 + \text{NH}_4\text{NO}_3$  occurs, presumably through catalyst interactions. The loss of  $^{18}\text{O}$  suggests exchange of surface oxygens of the catalyst through  $\text{HNC}^{18}\text{O}$  in the manner postulated for the disproportionation to  $\text{CO}_2$ .

Although the specific mechanism accepted may not be critical, it is apparent that production of guanidine nitrate from urea-ammonium nitrate depends on the specific function of the catalyst to direct the reaction of the initial decomposition products of urea toward formation of guanidine nitrate and to avoid the thermal conversion of these intermediates to triazines.

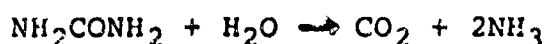
Additional references on this subject were noted<sup>33-37</sup>.

## II. Reactions of Urea

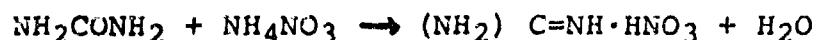
The reactions of urea have been discussed in the first section as they pertain directly to the preparation of guanidine nitrate. Specific reactions will be discussed in more detail here in relation to by-product formation.

### A. Hydrolysis

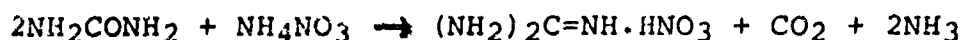
Hydrolysis of urea is the most important reaction of urea in the presence of water at elevated temperatures:



This reaction will generally be superimposed on other urea reactions if water is present. Thus the formation of guanidine nitrate:



becomes:



Hydrolysis is more rapid than biuret formation at 80°C.<sup>38</sup> and this is also undoubtedly true at the somewhat higher temperatures<sup>9</sup> (ca. 110°C.) at which the urea-ammonium nitrate feed is stored in current Hercules work on production of guanidine nitrate from urea. The hydrolysis reaction causes yield loss but reactions to form urea condensation products could cause product contamination.

General references to urea hydrolysis are listed<sup>39-44</sup>.

### B. Cyanic Acid and Cyanates

The dissociation of urea into cyanic acid and ammonia has been discussed as the first step in reactions of urea at elevated temperatures. This section will discuss references more specific to cyanic acid and cyanates.

The structure  $\text{HN}=\text{C}=\text{O}$  in straight line arrangement was indicated by Raman spectra<sup>45</sup>. Existence of  $\text{HOCN}$  has also been shown<sup>46</sup>. Hydrolysis of  $\text{HNCO}$  and  $\text{NCO}^-$  to give  $\text{NH}_4^+$  and  $\text{CO}_2$  and  $\text{NH}_3$  and  $\text{HCO}_3^-$ , respectively, has been studied<sup>46,47</sup>.

Conversion of urea to alkali metal cyanates has been cited earlier<sup>25-27,48</sup> as has isolation of  $\text{HNCO}$ <sup>21-24</sup>. Initial formation of  $\text{HNCO}$  from urea and subsequent reaction to produce biuret and triazine products will be involved in discussions of these materials in subsequent sections.

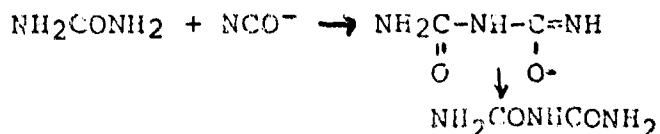


### C. Biuret and Triuret

Formation of biuret from aqueous urea solutions on heating was shown<sup>50</sup> but this reaction was accompanied by hydrolysis.

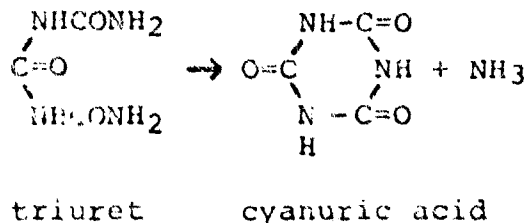
The rate of formation of biuret from urea increases with increasing temperature up to 170°C.<sup>7,38</sup>. A maximum was reached initially at 200°C. after which a decrease in amount of biuret occurred<sup>51</sup>. At 170°C. biuret was reported to begin to decompose to urea and cyanic acid<sup>52</sup>. The decrease in biuret was observed at 180 and 193°C.<sup>53</sup> and biuret formation was reported to be reversible above the melting point, 193°C.<sup>16,17</sup>

An important reference summarizes the changes which occur in the thermal decomposition of urea<sup>30</sup>. Infrared spectra showed that a new band appeared at 2170 cm<sup>-1</sup> at the melting point of urea; it disappeared at 160° and then reappeared at 180°C., the temperature at which biuret begins to decompose. This band disappeared at higher temperatures and reappeared at the melting point of triuret. This band was assigned to cyanate ion thus deduced to be present at the melting points of urea, biuret, and triuret. Formation of the cyanate ion (or HNCO) was confirmed by amination of biuret and triuret in an autoclave at 190°C. to give urea as the sole product. HNCO was found in the gas phase over melts of all three substances. The authors suggest the following course of the reaction:

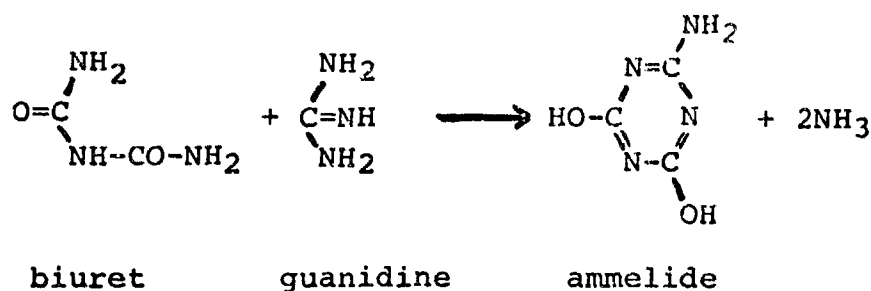


Triuret is postulated to form similarly.

Pyrolysis of triuret yielded only 15-20% of urea. It was suggested that the energetically more favorable ring closure to cyanuric acid occurs instead of complete reversal of the condensation.



The reaction of guanidine with biuret to form ammelide was postulated, supported by increased ammelide yield on addition of guanidine.



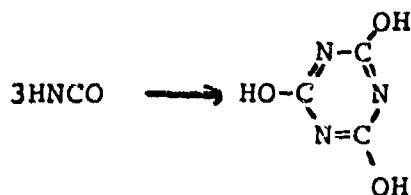
Triuret is formed on pyrolysis of urea in thin films<sup>13, 56</sup> but more readily in the presence of acid catalysts<sup>17, 54, 55</sup>.

Thus any biuret and triuret formed in the guanidine nitrate process could be converted back to urea and cyanic acid; the work cited suggests the additional possibilities of conversion of biuret to ammelide and of triuret to cyanuric acid. If appreciable amounts of biuret or triuret build up in the Hercules urea-ammonium nitrate feed, there would be a possibility of yield loss by formation of ammelide or cyanuric acid. However at the temperature of 110°C., build-up of more than a few percent of biuret is unlikely<sup>8</sup>. Appreciable triuret would not be expected.

Processes of preparation of biuret from urea are described in a number of references<sup>8, 9, 57-62</sup>. Suppression of biuret formation in urea on storage by the use of  $\text{NH}_4$  molybdate or  $\text{NH}_4\text{H}_2\text{PO}_4$  as additives has been reported<sup>63</sup>. Biuret has been eliminated from urea by ammonolysis<sup>64, 65</sup>. Urea increases the solubility of biuret in the system water-urea-biuret<sup>66</sup>. Biuret forms a borate with  $\text{H}_3\text{BO}_3$ <sup>67</sup>. Use of biuret as a fertilizer for turfgrass is described; it causes injury for a short time then is a useful source of nitrogen<sup>68</sup>.

#### D. Cyanuric Acid

As stated earlier, cyanuric acid is formed by thermal decomposition of urea at about 200°C. through the trimerization of  $\text{HNCO}$ .



cyanuric acid

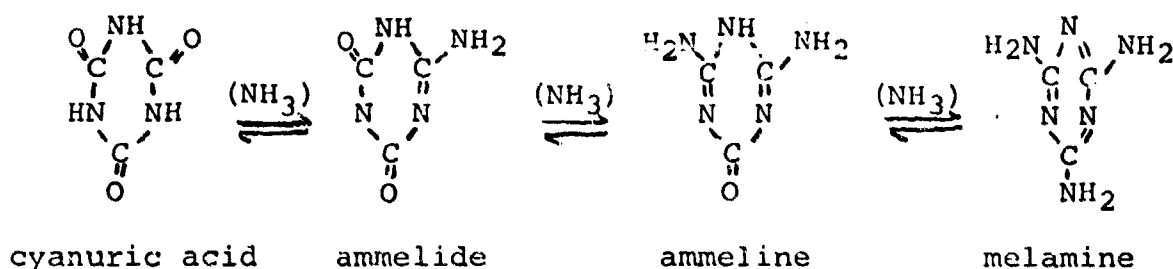
Formation of cyanuric acid is facilitated by removal of ammonia. Specific preparations involved: an ammonium halide with urea<sup>69</sup>,  $\text{H}_2\text{SO}_4$  as a catalyst<sup>11, 70</sup>, a phenolic solvent<sup>10</sup>, a fluidized bed

reaction<sup>71</sup>, use of HCl to lower the partial pressure of  $\text{NH}_3$ <sup>72</sup>, and mixtures of cyanuric acid and urea<sup>12,14</sup>. The reaction was carried out in vacuo at 280-300°C.<sup>26,73</sup> By-products, ammelide, ammeline, and melamine decreased with decreasing pressure. These by-products were stated to be formed by reaction of cyanuric acid with  $\text{NH}_3$ . This has been verified by reaction of cyanuric acid with  $\text{NH}_3$  at 270°C./80 atm.<sup>75</sup>

Above 300° cyanuric acid will decompose<sup>12</sup>. Temperatures in the 270°-300°C. range for urea pyrolysis give ammelide and ammeline rather than cyanuric acid<sup>19</sup>. Temperatures above 350°C. are used in the synthesis of melamine to avoid cyanuric acid formation<sup>74</sup>.

#### E. Ammelide and Ammeline

The cyanuric bases have frequently been assumed to be formed by amidation of cyanuric acid<sup>17</sup>.



These relationships can be demonstrated at temperatures of 250° and above. Ostrogovich and Bacalogu<sup>17</sup>, however, demonstrated the independent formation of each of these triazines at temperatures in the range 160-200°C. It thus seems likely<sup>15</sup> that intermediates such as the postulated cyanamide, or preferably a carbodiimide complex, react to form the ammelide, ammeline, and melamine at lower temperatures.

Direct formation of ammelide and ammeline from urea at 270-300°C. is reported<sup>19</sup>. In pyrolysis of urea at 280-320°C., yields of ammelide and ammeline decreased with decreasing pressure<sup>26,73</sup>. Preparation from cyanuric acid is described<sup>75</sup>. Usefulness of ammelide as a slow-release fertilizer has been demonstrated<sup>76</sup>. Spectrophotometric methods of analysis have been reported<sup>77,78</sup>.

#### F. Ammonium Nitrate-Urea Systems

Inasmuch as a urea-ammonium nitrate feed is used for guanidine nitrate preparation, references were sought which would indicate possible effects of one component on the reactivity of the other. The system  $\text{NH}_4\text{NO}_3 \cdot \text{CO}(\text{NH}_2)_2 \cdot \text{H}_2\text{O}$  was studied<sup>79</sup>. Compounds  $\text{NH}_4\text{NO}_3 \cdot \text{CO}(\text{NH}_2)_2$  and  $\text{NH}_4\text{NO}_3 \cdot 2\text{CO}(\text{NH}_2)_2$  appear to exist in solution. Phase diagrams for  $\text{NH}_4\text{NO}_3 \cdot \text{CO}(\text{NH}_2)_2$  were reported<sup>80</sup>.

Addition of urea decreased the acidity of ammonium nitrate and decreased nitrogen losses 300-500%<sup>81</sup>. Thermal decomposition of ammonium nitrate during its preparation is reported to be inhibited by urea<sup>82</sup>. Urea (0.1-0.3%) added directly to HNO<sub>3</sub> in the preparation of NH<sub>4</sub>NO<sub>3</sub> from NH<sub>3</sub> and HNO<sub>3</sub> eliminated the harmful effects of nitrogen oxides and Cl<sup>-</sup> ions and inhibited the thermal decomposition of NH<sub>4</sub>NO<sub>3</sub> during evaporation<sup>85</sup>. The presence of <0.7% urea in NH<sub>4</sub>NO<sub>3</sub> had no harmful effect on physiochemical or mechanical properties. Amounts of urea >1.5% increased hygroscopicity and decreased particle strength<sup>84</sup>.

The presence of NH<sub>4</sub>NO<sub>3</sub> in the pyrolysis of urea led to an increase in the content of cyanuric acid and a decrease in the amounts of ammeline, ammelide, and melamine<sup>83</sup>. The effect was attributed to formation and pyrolysis of urea nitrate.

#### G. Boric Acid Systems

The presence of boric acid in stabilizers for ammonium nitrate led us to note references of possible interest.

In the H<sub>3</sub>BO<sub>3</sub>-CO(NH<sub>2</sub>)<sub>2</sub> system, a compound was formed, H<sub>3</sub>BO<sub>3</sub>·2CO(NH<sub>2</sub>)<sub>2</sub>, melting point 79.1°C.<sup>86</sup>

Heating 1 mole of H<sub>3</sub>BO<sub>3</sub> and 2 moles of urea at about 60°C. gave a glass which decomposed above 165°C. to give BNO, stable to 1300°C. Passage of NH<sub>3</sub> over BNO at 500-950°C. gave relatively pure boron nitride, BN<sup>87</sup>.

A melamine synthesis catalyst, more or less equivalent to silica gel, termed boron phosphate, was made from 100 g. boric acid and 210 g. phosphoric acid<sup>98</sup>. The mixture solidified on standing at room temperature and was converted to catalyst by heating to 350°C.

### III. Formation of Melamine from Urea

In recent years, undoubtedly the most active area of research on reactions involving thermal decomposition of urea has been on processes for melamine from urea in eventually successful attempts to get away from dependence on calcium cyanamide and dicyanodiamide, "dicy". The first phase of this work from about 1950 to 1965 involved pressure reactions<sup>88-99, 104, 105</sup>. Then low pressure reactions were developed, first in two steps involving formation of HNCO and leading this over a catalyst<sup>100, 101, 103, 106, 110</sup>. Direct utilization of urea then followed<sup>31, 70, 102, 107, 108, 109, 111-116</sup>.

As mentioned earlier, this reaction is analogous to guanidine nitrate production from urea, with the differences of higher temperature and substitution of NH<sub>3</sub> for NH<sub>4</sub>NO<sub>3</sub><sup>31, 111</sup>. Thus it utilizes a catalyst such as silica gel (also Al<sub>2</sub>O<sub>3</sub>, Al silica gel,

and B, Al, Fe, and Si phosphates) which must contain free hydroxyl groups at high temperatures. The first step is formation of HNCO which is complexed with the catalyst. The HNCO then undergoes disproportionation to form CO<sub>2</sub> and the reactive carbodiimide intermediate (HN=C=NH), which trimerizes to melamine.

The initial breakdown of urea and disproportion of HNCO on the catalyst are apparently the same for the melamine and guanidine nitrate processes. Then in the guanidine nitrate process, a large excess of ammonium nitrate and a carefully controlled temperature direct the reaction of the catalyst complex to guanidine nitrate. In the melamine process, temperatures >350°C. are used. The high temperature assures completeness of the urea breakdown and the HNCO disproportionation reaction, presumably increasing the concentration of the reactive carbodiimide intermediate. The high temperature also prevents formation of cyanuric acid and ammelide. The net result is trimerization of the intermediate to melamine with only traces of by-products.

#### IV. Silica Gel-Phosphate Reactions

It has been determined empirically that decreases in catalyst activity observed in the course of the studies at Hercules Kenvil Plant can apparently be attributed to the presence of diammonium phosphate in the stabilizer for the ammonium nitrate used. A brief search of the literature was therefore made in an attempt to determine whether such effects are known.

No specific references were found to interactions of phosphates with silica gel in the type of system involved. There are, however, numerous references to reactions of phosphates with mineral surfaces but generally with aluminosilicates rather than silica gel. Phosphate fixation by kaolinite (an aluminosilicate) was observed and explained in terms of a two-step precipitation of an aluminum phosphate<sup>117</sup>. Silica-alumina gels absorbed both NH<sub>4</sub><sup>+</sup> and HPO<sub>4</sub><sup>=</sup> from (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub> solutions<sup>118</sup>. Adsorption of phosphate on kaolinite was in other examples attributed to Al or Fe<sup>119-121</sup>.

Phosphoric acid impregnated silica showed infrared spectra attributed to phosphate interaction with surface hydroxyl groups<sup>122</sup>. Adsorption of orthophosphates on metal oxides was demonstrated; it was concluded that chemical bonds were formed at the reactive metal oxide sites<sup>123</sup>. A study of the nature of active sites concluded that silica gel acquires ion-exchange capacity and catalytic properties exclusively as a result of substitution of Al for protons in active -OH groups<sup>124</sup>. Surface hydroxylation of silica and the nature of the groups was reported<sup>125</sup>.

Russian workers<sup>125</sup> studied reaction of PCl<sub>3</sub> with -OH groups on silica gel at 180°C. Each PCl<sub>3</sub> reacted with approximately 3 hydroxyl groups, with about 90% of the surface hydroxyls being susceptible to this reaction. This reaction is the closest to the type of reaction we would postulate to explain the effect of diammonium phosphate on catalytic activity. In fact, if diammonium

phosphate were as reactive as  $\text{PCl}_3$ , we would have a satisfactory explanation. However, in the present status of our information, we can only conclude that the literature is not inconsistent with surface reaction of the phosphate with -OH groups to inactivate the catalytic sites on the silica gel.

## V. Summary and Conclusions

Little new information was found on the process for guanidine nitrate from urea and ammonium nitrate, but reaction characteristics and reaction mechanisms have been reviewed. The catalytic reaction with silica gel leads to the formation of guanidine nitrate and small amounts of triazine by-products at temperatures which give cyanuric acid as the main product in a straight thermal reaction. The mechanism appears to involve: (1) formation of  $\text{HNCO}$  from urea; (2) complexing of  $\text{HNCO}$  with the catalyst, followed by disproportionation to  $\text{CO}_2$  and a reactive carbodiimide-catalyst complex; and (3) displacement of the carbodiimide by ammonium nitrate to give guanidine nitrate.

The current Hercules procedure of holding the urea-ammonium nitrate feed at about  $110^\circ\text{C}$ . for extended periods can be expected to involve the reactions: (1) hydrolysis of urea to give yield losses and (2) formation of biuret. An experimental check should be made of the biuret formed, but amounts in excess of 5% would not be expected. Formation of biuret is readily reversed at reaction conditions so that its formation in small amounts would not be a serious problem. Significant amounts of triazine products would not be formed at the feed temperature.

Cyanuric acid, ammelide, ammeline, and melamine can all form at the guanidine nitrate process temperature. Maintenance of catalyst activity, optimum reactant ratios, and temperatures as low as compatible with practical rates can be utilized to minimize these by-products.

Recently developed processes for production of melamine from urea and ammonia appear to involve the same initial steps as production of guanidine nitrate from urea and ammonium nitrate, namely, formation of  $\text{HNCO}$  from urea and disproportionation on the catalyst. The melamine process is run at temperatures  $>350^\circ\text{C}$ . which avoid formation of cyanuric acid, ammelide, and ammeline and give high concentrations of the reactive intermediate which then trimerizes to melamine.

Information on possible reactions of phosphates with silica gel was sought in view of the finding at Hercules Kenvil Plant that diammonium phosphate in the ammonium nitrate stabilizer decreases the activity of the catalyst. Adsorption of phosphates on mineral surfaces has frequently been reported but generally appears to involve Al or Fe in the mineral clays. Phosphoric acid-impregnated silica showed evidence of chemical reaction of phosphate groups with surface hydroxyls. Chemical reaction between  $\text{PCl}_3$  and hydroxyl groups of silica gel has been demonstrated and

offers an analogy to what appears to happen with diammonium phosphate. Specific references have not been located for reaction of phosphates with silica gel under conditions of the guanidine nitrate reactions. However, the information in the literature is not inconsistent with surface reaction of phosphate to inactivate the catalytic sites on silica gel.

### Bibliography

#### I. Guanidine Nitrate from Urea

1. F. Armstrong and R. T. M. Fraser, Explosive Research and Development Establishment, Ministry of Defense, Waltham Abbey, England, "The Silica Gel Process: Small Scale Studies. Part I - Comparison of Catalysts. Labelling Experiments". This report was received by C. H. Nichols of Picatinny Arsenal through Dr. Pearson of the British Embassy, Washington, D. C. on Feb. 24, 1972 and forwarded to Hercules on Feb. 25, 1972. (Unclassified)
2. L. G. Boatright and J. S. Mackay (American Cyanamid), U.S. Patent 2,783,276 (1957).
3. J. S. Mackay (Pittsburgh Coke & Chemical Co.), "Guanidine Compounds", U.S. 2,949,484, Aug. 16, 1960. C.A. 55, 9288 (1961).
4. E. Roberts and T. Martin (to Minister of Aviation in Her Majesty's Government of the United Kingdom of Great Britain and Northern Ireland), U.S. Patent 3,043,878 (1962).
5. S. N. Kazarnovskii and R. I. Spasskaya, "Preparation of Salts of Guanidine from Urea and Ammonium Salts in the Presence of Silica Gel", Zhur. Priklad. Khim. 34, 2079-84 (1961). C.A. 56, 2326 (1962).
6. A. Sonn, "Biuret and Triuret from Urea", Ger. 726,290, Aug. 27, 1942. C.A. 37, 6281 (1943).
7. R. C. Shen (U.S. Ind. Chemicals Co.), "Rate of Biuret Formation from Urea", J. Agr. Food Chem. 7, 762-3 (1959). C.A. 54, 3195 (1960).
8. L. Jaeger, J. Gottfried, J. Nyvit, and J. Sura, "The Kinetics of Biuret Formation from Urea", Chem. Prumysl 15(1), 4-7 (1965). C.A. 62, 13004 (1965).
9. C. Merli, C. Galipo, and D. Ferroni (Montecatini), "Preparation of Biuret of High Purity", Ital. 698,339, Nov. 18, 1965. C.A. 67, 108269 (1967).
10. L. J. Christmann (American Cyanamid Co.), "Cyanuric Acid from Urea", U.S. 2,822,363, Feb. 4, 1958. C.A. 52, 10223 (1958).

11. N. I. Malkina and S. N. Kazarnovskii, "Synthesis of Cyanuric Acid from Urea. I.", Zhur. Priklad. Khim. 34, 1583-7 (1961). C.A. 55, 27362 (1961).
12. H. A. Baskin (W. R. Grace & Co.), "Production of Cyanuric Acid from Urea", U.S. 3,236,845, Feb. 22, 1966. C.A. 64, 15901 (1966).
13. R. I. Spasskaya and S. N. Kazarnovskii, "Triuret", U.S.S.R. 252,327, Sept. 22, 1969. C.A. 72, 54820 (1970).
14. F. Suzuki and T. Tosen (Japan Light Metal Co., Ltd.), "Cyanuric Acid by Thermal Decomposition of Urea", Japan. 69 00,234, Jan. 8, 1969. C.A. 70, 87858 (1969).
15. R. I. Spasskaya and S. N. Kazarnovskii, "Reaction of Urea with Ammonium Salts in the Presence of Silica Gel", Zh. Prikl. Khim. 35, 1842-6 (1962). C.A. 58, 6828 (1963).
16. K. Alaminov, A. Vblcheva, and St. Georgieva, "Formation of Biuret and Possibilities for Its Decrease in the Production of Carbamide", Khim. i Ind. (Sofia) 32, No. 3, 71-4 (1960). C.A. 55, 3426 (1961).
17. G. Ostrogovich and R. Bacaloglu, "Kinetic Study on the Thermolysis and the Subsequent Transformations of Urea. II.", Rev. Roumaine Chim. 10(11), 1111-23 (1965) (Ger.); Studii Cercetari Chim. 13(11), 1165-76 (1965) (Rom). C.A. 64, 15700 (1966).
18. G. Ostrogovich and R. Bacaloglu, "Kinetic Study on the Thermolysis and the Subsequent Transformations of Urea. III.", Rev. Roumaine Chim. 10(11), 1125-35 (1965) (Ger.); Studii Cercetari Chim. 13(11), 1177-86 (1965) (Rom.). C.A. 64, 15700 (1966).
19. L. J. Beckham (Allied Chemical & Dye Corp.), "Ammelide and Ammeline", U.S. 2,572,587, Oct. 23, 1951. C.A. 46, 6163 (1952).
20. N. P. Shishkin and A. I. Finkel'shtein, "In Vacuo Pyrolysis of Urea", Tr. Khim. Khim. Tekhnol. 1969, (1), 188-90. C.A. 73, 24736 (1970).
21. Oesterreichische Stickstoffwerke A.-G., "Cyanic Acid from Urea", Belg. 621,602, Feb. 21, 1963. C.A. 59, 1307 (1963).
22. E. S. Roberts and L. J. Christmann (Carbogen Corp.), "Cyanic Acid", Ger. 1,159,411, Dec. 19, 1963. C.A. 60, 10254 (1964).
23. Oesterreichische Stickstoffwerke A.-G., "Cyanic Acid from Urea", Neth. Appl. 6,500,131, July 15, 1965. C.A. 63, 17916 (1965).



24. A. Schmidt, F. Weinrotter, and W. Mueller (Lentia G.m.b.H.), "Process for Cyanic Acid from Urea", Ger. 1,204,643, Nov. 11, 1965. C.A. 64, 3096 (1966).
25. E. Inaba, S. Uesugi, and Y. Enoeda (Shinetsu Chemical Industries Co.), "Alkali Cyanate", Japan. 4030('55), June 14, 1955. C.A. 51, 14217 (1957).
26. D. O. DePree and K. L. Lindsay (Ethyl Corp.), "Metal Cyanates", U.S. 2,801,154, July 30, 1957. C.A. 51, 18507 (1957).
27. F. O. Barrett and J. Kamlet (Emery Industries, Inc.), "Conversion of Urea to Metal Cyanates", U.S. 2,899,198, June 2, 1959. C.A. 53, 17449 (1959).
28. A. G. Koryakin, V. A. Gal'perin, A. N. Sarbaev, and A. I. Finkel'shtein, "Thermographic Analysis of Urea and Products of Its Pyrolysis", Zh. Org. Khim. 7(5), 972-7 (1971). C.A. 75, 54200 (1971).
29. J. Gisbier and J. Koch, "Pyrolysis of Urea in a Low-Temperature Plasma", Z. Chem. 11(12), 465 (1971). C.A. 76, 63932 (1972).
30. V. A. Gal'perin, A. I. Finkel'shtein, and N. P. Shishkin, "Mechanism of the Thermal Decomposition of Urea, Biuret, and Triuret", Zh. Vses. Khim. Obshchest. 17(3), 359-60 (1972). C.A. 77, 93342 (1972).
31. A. Schmidt (Oesterr. Stickstoffwerke A.-G.), "Reaction Mechanism for Melamine Formation from Isocyanic Acid", Monatsh. Chem. 99(2), 664-71 (1968). C.A. 68, 95792 (1968).
32. R. K. Iler (Du Pont), "Esterifying the Reactive Siliceous Surfaces of Supercolloidal Substrates", U.S. 2,657,149, Oct. 27, 1953. C.A. 48, 2336 (1954).
33. G. W. Watt and R. G. Post, "Guanidine from Urea and Ammonia", Ind. Eng. Chem. 45, 846-9 (1953). C.A. 48, 1276 (1954).
34. J. L. Boivin, "The Preparation of Guanidine from Urea, Ammonium Chloride, Aluminum Sulphate, and Ammonia under Pressure", Can. J. Chem. 33, 1467-72 (1955). C.A. 50, 11246 (1956).
35. R. I. Spasskaya and S. N. Kazarnovskii, "A Continuous Method for the Production of Guanidine from Urea", Khim. Prom. 1963(7), 488-91. C.A. 60, 1580 (1964).
36. R. Bacaloglu and G. Ostrogovich (Romania Chemical Plant), "Catalyst for the Thermal Dehydration or Disproportionation of Amide-Type Compounds", Rom. 51,080, July 24, 1968. C.A. 70, 41266 (1969).

37. R. Bacaloglu and G. Ostrogovich (Romania, Chemical Combine), "Catalyst for the Thermal Dehydration or Disproportionation of Amide-Type Compounds", Rom. 51,083, July 19, 1968. C.A. 70, 41267 (1969).

## II. Reactions of Urea

### A. Hydrolysis

38. C. E. Redemann, F. C. Riesenfeld, and F. S. LaViola, "Formation of Biuret from Urea", Ind. Eng. Chem. 50, 633-6 (1958). C.A. 52, 11317 (1958).
39. O. Alpaut, "The Rate of Decomposition of Urea", Communs. fac. sci. univ. Ankara 7B, No. 1, 28-44 (1956). C.A. 52, 19939 (1958).
40. W. H. R. Shaw and J. J. Bordeaux, "The Decomposition of Urea in Aqueous Media", J. Am. Chem. Soc. 77, 4729-33 (1955). C.A. 50, 3045 (1956).
41. Y. Kauko and O. Alpaut, "Decomposition of Urea", Naturwissenschaften 42, 390 (1955). C.A. 51, 17760 (1957).
42. Same as reference 39.
43. R. B. Moodie and D. W. Farlow, "Hydrolysis of Amides, Esters, and Related Compounds in Acid Solution. III. Ureas", J. Chem. Soc. B 1971, (3), 407-10. C.A. 74, 111207 (1971).
44. H. L. Welles, A. R. Giaquinto, and R. E. Lindstrom, "Degradation of Urea in Concentrated Aqueous Solution", J. Pharm. Sci. 1971, 60(8), 1212-16. C.A. 75, 107915 (1971).

### B. Cyanic Acid and Cyanates

45. L. Birckenbach, H. Kolb. and J. Goubeau, "Pseudohalides. XXIX. Preparation, Reactions and Tautomers of Cyanates and Cyanic Acid", Ber. 68B, 895-912 (1935). C.A. 29, 4687 (1935).
46. M. B. Jensen, "Kinetics of the Decomposition of Cyanic Acid", Acta Chem. Scan. 12, 1657-70 (1958). C.A. 54, 2906 (1960).
47. J. R. Marier and D. Rose, "Determination of Cyanate, and a Study of Its Accumulation in Aqueous Solutions of Urea", Anal. Biochem. 7(3), 304-14 (1964). C.A. 60, 8334 (1964).
48. D. O. De Pree and E. B. Oldenburg (Ethyl Corp.), "Metal Cyanates", U.S. 2,729,541, Jan. 3, 1956. C.A. 50, 6001 (1956).
49. N. Groving and A. Holm, "Alkyl Cyanates. V. Existence of Cyanic Acid, HOCN", Acta Chem. Scan. 19(7), 1768-9 (1965). C.A. 64, 6059 (1966).

Also see references 21-27.

C. Biuret and Triuret

50. T. Nukada, "Aqueous Solution of Urea and the Biuret Reaction", Japan. J. Pharm. Chem. 23, 391-2 (1951). C.A. 46, 10107 (1952).
51. S. N. Kazarnovskii and N. I. Malkina, "Mechanism of the Reaction of Thermal Decomposition of Urea under the Pressure of the Gases Formed", Zhur. Priklad. Khim. 31, 452-8 (1958). C.A. 52, 17104 (1958).
52. N. I. Malkina and S. N. Kazarnovskii, "The Study of the Mechanism of Formation of By-Products During the Synthesis of Cyanuric Acid from Urea", Trudy Gor'kovsk. Politekh. Inst. 13, No. 5, 32-6 (1957). C.A. 54, 1538 (1960).
53. A. Baranski, E. Blasiak, and Z. Matuszewski, "The Reactions of Synthesis, Decomposition and Condensation of Urea", Chim. Ind. (Paris) 93(4), 408-12 (1965). C.A. 63, 11306 (1965).
54. G. Ostrogovich, R. Bacaloglu, A. Nemes, and M. Moraru, "Kinetic Study on the Thermolysis and the Subsequent Transformations of Urea. I.", Acad. Rep. Populare Romine, Baza Cercetari Stiint. Timisoara, Studii Cercetari, Stiinte Chim. 8, No. 1-2, 59-78 (1962). C.A. 59, 2628 (1963).
55. R. Colin Haworth and F. G. Mann, "Some Properties of Urea, Biuret and Triuret", J. Chem. Soc. 603-6 (1943). C.A. 38, 1475 (1945).
56. E. V. Lassak, "Autocondensation of Urea at 105-110°", J. Proc. Roy. Soc. N. S. Wales 100(3-4), 179-80 (1966). C.A. 68, 87276 (1968).
57. J. Harmon (Du Pont), "Biuret Production from Urea", U.S. 2,145, 392, Jan. 31, 1939. C.A. 33, 3399 (1939).
58. M. Mikhailov and K. Alaminov, "Corrosion of Some Stainless Steels and Al during the Pyrolysis of Urea in a High Boiling Oil Medium", Khim. Ind. (Sofia) 38(1), 19-21 (1966). C.A. 65, 401 (1966).
59. D. G. Shipley (ICI), "Urea Pyrolysis", Brit. 1,155,907, June 25, 1969. C.A. 71, 60784 (1969).
60. R. Bacaloglu and G. Ostrogovich, "The Synthesis of Biuret from Urea", Rev. Chim. (Bucharest) 11, 332-4 (1960). C.A. 57, 12315 (1962).
61. A. F. Beale, Jr., and J. M. Lee (Dow Chemical Co.), "Biuret from Urea by Pyrolysis", Ger. Offen. 2,049,294, Apr. 22, 1971. C.A. 74, 141038 (1971).
62. A. F. Beale, Jr. and J. M. Lee (Dow Chemical Co.), "Biuret Manufacture by Urea Pyrolysis", Fr. 2,065,102, Aug. 27, 1971. C.A. 76, 126431 (1972).

63. Stamicarbon N.V., "Suppression of Biuret Formation in Urea", Dutch 94,646, June 15, 1960. C.A. 55, 14314 (1961).
64. E. Sacher (Oesterreichische Stickstoffwerke A.-G.), "Removal of Biuret from Urea", Austrian 219,051, May 24, 1960. C.A. 56, 12749 (1962).
65. V. I. Kucheryavii, L. N. Al'mshuler, L. N. Erastov, "Ammonolysis of Biuret in Aqueous Solutions of Urea", Zh. Prikl. Khim. (Leningrad) 41(9), 2097-8 (1968). C.A. 70, 19319 (1969).
66. M. DeMalde, "The System Water-Urea-Biuret", Chimica e industria (Milan) 38, 571-5 (1956). C.A. 51, 61 (1957).
67. V. I. Bairak, M. S. Malinovskii, and E. A. Makarova, "Biuret Borate", U.S.S.R. 298,533, Mar. 16, 1971. C.A. 75, 88155 (1971).
68. R. W. Starostka and K. C. Clark, "Greenhouse Evaluation and Nitrification Characteristics of Biuret and Urea-Biuret Mixtures", Agr. Chemicals 10, No. 10, 49-50, 103-4 (1955). C.A. 50, 520 (1956).

Also see references 7, 8, 13, 16, 18, 30, and 38.

#### D. Cyanuric Acid

69. J. S. Mackay (American Cyanamid), "Cyanuric Acid", U.S. 2,527,316, Oct. 24, 1950. C.A. 45, 2513 (1951).
70. W. F. Marzluff and L. H. Sutherland (American Cyanamid Co.), "Cyanuric Acid", U.S. 2,768,167, Oct. 23, 1956. C.A. 51, 4665 (1957).
71. A. Schmidt, F. Weinrotter, and W. Mueller (Lentia G.m.b.H.), "Cyanuric Acid from Urea", Ger. 1,179,215, Oct. 8, 1964. C.A. 62, 4042 (1965).
72. F. J. Schiltknecht, "Reaction Mechanism of the Pyrolysis of Urea to Cyanuric Acid", Promotionsarb. (Zurich) 3403, 92 pp. (1963). C.A. 63, 5647 (1965).
73. N. P. Shishkin, A. I. Finkel'shtein, "Formation of By-Products During the Preparation of Cyanuric Acid from Urea", Zh. Prikl. Khim. (Leningrad) 42(2), 471-5 (1969). C.A. 71, 22115 (1969).
74. A. Schmidt, "Chemical Research in Austrian Industry. I. Technical Processing Problems in the Production of Melamine from Urea at Atmospheric Pressure", Oesterr. Chem.-Ztg. 68(6), 175-9 (1967). C.A. 67, 116874 (1967).
75. V. A. Gal'perin and A. I. Finkel'shtein, "Reaction of Cyanuric Acid and Its Amides with Ammonia", Khim. Geterotsikl. Soedin. 7(7), 1002 (1971). C.A. 76, 14504 (1972).

Also see references 10-12, 14, 19, and 26.

E. Ammelide and Ammeline

76. G. L. Terman, J. D. DeMent, C. M. Hunt, J. T. Cope, Jr., and L. E. Ensminger, "Crop Response to Urea and Urea Pyrolysis Products", J. Agr. Food. Chem. 12(2), 151-4 (1964). C.A. 60, 11334 (1964).
77. V. A. Gal'perin, T. N. Roginskaya, "Determination of Amino Oxo Derivatives of Symtriazine and Nitrate Ion Present Together", Zavod. Lab. 34(11), 1324-5 (1968). C.A. 70, 64144 (1969).
78. S. G. Farrow, S. R. Hill, and J. M. Skinner, "High Precision Spectrophotometry. II. Determination of Ammelide, Ammeline, and Melamine in the Thermal Decomposition Products of Urea", Analyst (London) 97(1150), 42-51 (1972). C.A. 76, 80876 (1972).

Also see references 15, 17, 19, 73, and 75.

F.  $\text{NH}_4\text{NO}_3$ -Urea System

79. C. S. Pande, "Formation of Complex Compounds Between Ammonium Nitrate and Urea. The System:  $\text{NH}_4\text{NO}_3\text{-CO}(\text{NH}_2)_2\text{-H}_2\text{O}$  (Conductivity and Viscosity)", Z. anorg. u. allgem. Chem. 280, 157-60 (1955). C.A. 50, 1510 (1956).
80. D. Trandafelov and T. Kovachev, "Molten Salt Systems with Ammonium Nitrate as the Main Component. I.", Izv. Inst. Obshta Neorg. Khim., Bulg. Akad. Nauk. 5, 25-36 (1967). C.A. 69, 90302 (1968).
81. S. Popov, V. Vasilev, and A. Angelov, "Lowering Ammonium Nitrate Settling", Khim. Ind. (Sofia) 43(10), 463-5 (1971). C.A. 76, 156207 (1972).
82. Y. Kil'man, "Inhibition of the Thermal Decomposition of Ammonium Nitrate", U.S.S.R. 191,498, Jan. 26, 1967. C.A. 68, 31636 (1968).
83. N. P. Shishkin, A. I. Finkesl'shtein, and V. I. Zagranichnyi, "Effect of Acid Additives on the Pyrolysis of Urea", Zh. Prikl. Khim. (Leningrad) 45(2), 433-4 (1972). C.A. 77, 4646 (1972).
84. Y. B. Gradinar, "Effect of Urea Additives on Physicochemical Properties of Ammonium Nitrate", Tr. Nauch.-Issled. Proekt. Inst. Azotn. Prom. Prod. Org. Sin. 1971, No. 6, 351-6. C.A. 77, 64085 (1972).
85. Y. I. Kil'man, G. S. Barkhatova, and M. A. Kuzina, "Thermal Decomposition of Ammonium Nitrate in the Presence of Urea", Tr. Nauch.-Issled. Proekt. Inst. Azotn. Prom. Prod. Org. Sin. 1971, No. 6, 321-33. C.A. 77, 60771 (1972).

### G. Boric Acid Systems

86. V. G. Skvortsov and I. G. Druzhinin, "Solubility Polytherm of Boric Acid-Water and Potassium Metaborate-Water Binary Systems and the Phase Diagram of  $\text{CO}(\text{NH}_2)_2$ -Boric Acid", Uch. Zap., Chuvash. Gos. Pedagog. Inst. 1969, No. 29, 150-63. C.A. 74, 116570 (1971).
87. T. E. O'Connor, "Synthesis of Boron Nitride", J. Am. Chem. Soc. 84, 1753-4 (1962). C.A. 56, 3061 (1962).

Also see reference 98.

### 1III. Melamine from Urea

88. Monsanto Chemical Co., "Melamine", Brit. 644,374, Oct. 11, 1950. C.A. 45, 4274 (1951).
89. W. F. Gresham (du Pont), "Titanium Apparatus for Manufacture of Melamine", U.S. 2,644,820, July 7, 1953. C.A. 47, 9070 (1953).
90. R. S. Hood (Monsanto Chemical Co.), "Melamine", U.S. 2,776,284, Jan. 1, 1957. C.A. 51, 6107 (1957).
91. Bergwerksgesellschaft Hibernia Akt.-Ges., "Melamine", Brit. 754,720, Aug. 8, 1956. C.A. 51, 7671 (1957).
92. Sddeutsche Kalkstickstoff-Werke A.-G., "Melamine from Urea", Ger. 836,354, Apr. 10, 1952. C.A. 51, 11759 (1957).
93. M. Mikhailov and K. Alaminov, "Preparation of Melamine from Urea", Khim. Prom. 1961, 319-25. C.A. 55, 25351 (1961).
94. M. Mikhailov and K. Alaminov, "Preparation of Melamine from Urea", Khim. Prom. 1961, 805-6. C.A. 57, 11200 (1962).
95. A. Brenman and M. Weinberg, "The Synthesis of Melamine from Urea", Rev. Chim. (Bucharest) 12, 652-5 (1961). C.A. 56, 15114 (1962).
96. G. Naumov, "Synthesis of Melamine from Urea", Khim. Ind. (Sofia) 33, 190 (1961). C.A. 57, 16619 (1962).
97. Z. Jezic, "Preparation of Melamine from Urea", Croat. Chem. Acta 34, 203-9 (1962). C.A. 58, 11362 (1963).
98. O. B. Claren and L. Unterstenhoefer (Badische Anilin- & Soda-Fabrik A.-G.), "Cyanuric Acid", Fr. 1,363,760, June 12, 1964. C.A. 60, 14693 (1964).
99. V. I. Zagranichnyi and O. S. Rukevich, "The Reaction-Equilibrium in the Formation of Melamine from Urea", Khim. Prom. 1965(3), 188-90. C.A. 62, 12385 (1965).

100. Oesterreichische Stickstoffwerke A.-G., "Melamine from Cyanic Acid", Neth. Appl. 6,412,596, May 2, 1966. C.A. 65, 8936 (1966).
101. A. Schmidt (Osterr. Stickstoffwerke A.-G.), "New OSW Process Makes Melamine Direct from Urea", Hydrocarbon Process. 45(11), 146-50 (1966). C.A. 66, 10906 (1967).
102. A. Schmidt, "Preparation of Melamine from Urea at Atmospheric Pressure", Chem. Ingr. Tech. 38(11), 1140-4 (1966). C.A. 66, 18700 (1967).
103. W. Boehler, W. Mueller, A. Schmidt, and F. Weinrotter, (Oesterreichische Stickstoffwerke A.-G.), "Melamine from Cyanic Acid", Brit. 1,047,095, Nov. 2, 1966. C.A. 66, 18727 (1967).
104. E. E. Jackson (Cominco Ltd.), "Preparation of Melamine from Urea", Can. 743,956, Oct. 4, 1966. C.A. 66, 28801 (1967).
105. Nisson Chemical Industries, Ltd., "Continuous Manufacture of Melamine from Urea", Fr. 1,483,116, June 2, 1967. C.A. 68, 13007 (1968).
106. Inventa A.-G. fuer Forschung und Patenverwertung, "Two-Stage Preparation of Melamine from Urea", Fr. 1,484,358, June 9, 1967. C.A. 68, 13008 (1968).
107. S. W. Tribit (American Cyanamid Co.), "Preparation of Melamine from Urea", U.S. 3,377,349, Apr. 9, 1968. C.A. 68, 105252 (1968).
108. E. K. Watson and J. M. Witheford (American Cyanamid Co.), "Melamine", U.S. 3,377,350, Apr. 9, 1968. C.A. 68, 114657 (1968).
109. G. Hamprecht, M. Schwarzmann, "Synthesis of Melamine from Urea by a Pressureless Single-Stage Process", Chem.-Ing.-Tech. 40(9-10), 462-4 (1968). C.A. 69, 27388 (1968).
110. M. Manes (Chemical Construction Corp.), "Synthesis of Melamine", U.S. 3,386,999, June 4, 1968. C.A. 69, 27463 (1968).
111. M. Schwarzmann, "Make Melamine at Atmospheric Pressure", Hydrocarbon Process. 48(9), 184-6 (1969). C.A. 71, 112893 (1969).
112. R. F. Hazelton (Allied Chemical Corp.), "Melamine", U.S. 3,470,163, Sept. 20, 1969. C.A. 71, 112990 (1969).
113. S. Furutani, K. Narizawa and M. Tanaka (Tohoku Fertilizer Co., Ltd.), "Melamine from Urea", Japan. 69 28,910, Nov. 26, 1969. C.A. 72, 31844 (1970).
114. S. Furutani, K. Narizawa and M. Tanaka (Tohoku Fertilizer Co., Ltd.), "Melamine from Urea", Japan. 69 28,909, Nov. 26, 1969. C.A. 72, 55512 (1970).

115. P. Ellwood, "Lower Investment, Easier Operation to Make Melamine", Chem. Eng. (New York) 77(23), 101-3 (1970). C.A. 74, 66116 (1971).
116. O. Rukevich and V. I. Zagranichnyi, "Reaction Equilibrium of the Formation of Melamine from Urea. I.", Zh. Prikl. Khim. (Leningrad) 44(5), 1132-7 (1971). C.A. 75, 7675C (1971).

Also see references 31 and 70.

#### IV. Silica Gel-Phosphate Reaction

117. P. F. Low and C. A. Black, "Reactions of Phosphate with Kaolinite", Soil Sci. 70, 273-90 (1950). C.A. 45, 4387 (1951).
118. C. J. Plank, "The Adsorption of Ions from Buffer Solutions by Silica, Alumina, and Silica-Alumina Gels", J. Phys. Chem. 57, 284-90 (1953). C.A. 47, 6214 (1953).
119. G. C. Russell and P. F. Low, "Reaction of Phosphate with Kaolinite in Dilute Solution", Soil Sci. Soc. Am. Proc. 18, 22-5 (1954). C.A. 48, 6636 (1954).
120. A. G. Scholten, "The Reaction of Phosphate with Mineral Surfaces and Iron Oxide Gels", Univ. Microfilms, Order No. 65-6238, 254 pp.; Dissertation Abstr. 25(12), 6949-50 (1965). C.A. 63, 10975 (1965).
121. R. M. Barrer and D. J. Marshall, "Chemistry of Soil Minerals. II. Reactions of Phosphates with kaolin and Faujasite", J. Chem. Soc. 1965(Nov.), 6621-8. C.A. 64, 1853 (1966).
122. M. J. D. Low and P. Ramamurthy, "Infrared Study of the Surface Properties of Phosphoric Acid Impregnated Silica", J. Phys. Chem. 72(9), 3161-7 (1968). C.A. 69, 89965 (1968).
123. D. R. Vissers, "Sorption of Orthophosphate on Crystalline Metal Oxides", J. Phys. Chem. 72(9), 3236-44 (1968). C.A. 69, 89966 (1968).
124. K. G. Miessnerov, "Nature of Active Sites of Aluminosilicate Catalysts", J. Catal. 13(2), 169-85 (1969). C.A. 70, 71378 (1969).
125. R. J. Passarelli, "Self-Diffusion Coefficients of Strontium in Agar Gels as Functions of Concentration and Temperature", Diss. Abstr. B 29(8), 2388 (1969). C.A. 70, 91108 (1969).
126. C. G. Armistead, A. J. Tyler, F. H. Hambleton, S. A. Mitchell, and J. A. Hockey, "Surface Hydroxylation of Silica", J. Phys. Chem. 73(11), 3947-53 (1969). C.A. 72, 6453 (1970).